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THE
ATOMIC THEORY

BY

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PREFACE

TO

THE THIRD EDITION

A FEW LINES of introduction were written for the First Edition of this work, but their appearance was impossible, since the book had to be published at a certain date. It is now the duty of the Author to thank the public for the favourable reception accorded to this little book, in spite of the abstract nature of the subjects which are discussed in it. An endeavour has been made to reduce them to their simplest terms by depriving them as much as possible of the severe garb of formulæ and by arranging them in their historical order. Much useful information has been derived from the works of Hermann Kopp, who has discussed with so much ability and impartiality a great mass of ancient and modern work, only omitting his own.

The only change introduced into this edition, one which is worthy of notice, relates to the history of the theory of atomicity.

We have mentioned, on page 198, Frankland as the first author of the idea of the saturation of elements. It has seemed just to add that this idea, which was developed later as a consequence of the theory of the saturation of radicals, contained the germ of the idea of atomicity. It must be remembered that the latter is only the revived expression and complement of the theory of multiple proportions, as was remarked as early as 1864.

A. Wurtz

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THE ATOMIC THEORY.

BOOK I.

ATOMS.

CHAPTER I.

HISTORICAL INTRODUCTION—RICHTER—DALTON.

The hypothesis of atoms, put forward by the Greek philosophers, and revived in modern times by great thinkers, acquired a definite form at the beginning of this century. John Dalton was the first to apply it to the interpretation of the laws which he and Richter recognised as governing chemical combinations. Confirmed by the great discoveries of Gay-Lussac, Mitscherlich, Dulong and Petit, the hypothesis has assumed a definite form, connecting many various facts of a chemical and physical nature. Fundamentally it consists of modern ideas upon the constitution of matter.

In common with correct ideas, it has grown with time, and nothing has as yet happened to stop its progress; but, in common with all fruitful ideas, it has been an instrument of progress even in the hands of its detractors. The latter are now few, and the hypothesis seems to make a firm stand against the regular opposition of some and the subtle attacks of others. In these pages we propose to discuss both its historical evolution and its present form, and we shall thus show the influence it has exercised upon the progress of science since the beginning of the century.

Dalton revived the hypothesis of atoms to explain the fact that in chemical combinations elements unite in fixed proportions, and in certain cases in multiple proportions. He admitted that these proportions represent the relative weights of indivisible particles of the bodies, which particles are brought into contact and grouped by the fact of combination. This led to the consideration of atomic weights, and the idea of representing the composition of bodies by symbols which indicate both the nature and the number of these particles and the proportion of the elements entering into combination. We have here two things which must not be confounded—facts and an hypothesis. We shall retain the hypothesis as long as it gives a faithful interpretation of facts, and enables us to group them, to connect them together, and to anticipate fresh ones—as long, in fact, as it proves fertile. An hypothesis thus formed rises to the rank of a theory. We shall endeavour to show, in demonstrating its origin, progress, and results, that this is the case with Dalton's conception.

I.

Simple bodies combine in definite proportions. This is one of the most firmly established truths of natural philosophy. It includes the two following facts:—Firstly, the relative weight of combining bodies is always fixed in every combination; secondly, the numbers which express these relations are interproportional for all kinds of combinations. We must clearly understand the meaning of these propositions.

Two simple bodies unite so as to form a given compound. As long as the compound lasts the relative weights of the two elements will remain perfectly constant, whether the quantities acting upon each other have been great or small; the smallest particles, as well as the whole mass, will contain strictly proportional weights of these elements, which no physical circumstances, such as pressure or temperature, can modify. This is true for all kinds of combinations, the most simple as well as the most complicated. This fixity of the proportion in which bodies combine was acknowledged and admitted as a truth more than a century ago by some eminent chemists, and by all in the year 1806. Bergman was conscious of the truth, even if not logically convinced of it; in fact, the numerous quantitative analyses for which we are indebted to him would have been aimless or useless if he had been under the impression that the compounds he was analysing were formed in chance proportions. Lavoisier demonstrated in the clearest manner the fact of the constancy of the relations in which bodies combine. In every oxide, in every acid, he said, the relation of oxygen to the metal is constant; and this relation should be exactly determined for every oxygen compound. He admits, moreover, that the difference between the acids of sulphur and the oxygen compounds of nitrogen is due to the power possessed by these simple bodies of uniting with oxygen in several proportions, each degree of oxidation corresponding to a fixed and constant relation between the weights of the two elements. The law of fixity was thus distinctly admitted and clearly stated by Lavoisier; one step more, and he would have discovered the law of multiple proportions. He did not, however, make this decisive step. Even as regards the fixity of several proportions, though he was himself convinced of the fact, he was not successful in making it universally accepted. In the month of July 1799 his pupil Berthollet read at the Egyptian Institute, which was sitting at Cairo, a memoir entitled 'Researches upon the Laws of Affinity.' He there for the first time brought forward profound ideas upon the influence exercised by the physical condition, the cohesion, solubility, insolubility, and volatility of bodies upon the affinity and progress of chemical decompositions. Without denying the fixity of the composition of certain compounds, he attributed this fact to the chance influence of these physical conditions, which in some cases were constant, and would not allow that it partook of the character of a general law.

It is true, he said, that in sulphate of baryta the relation between the sulphuric acid and the baryta is constant, simply because the acid and base must unite in this precise and fixed proportion to form a salt of absolute insolubility. Thus, here as in many other cases, constancy of composition is dependent upon a physical property, cohesion—in other words, the insolubility of the sulphate of baryta. But the rule is as follows: Chemical combinations take place in proportions which may vary within certain limits.

A salt formed by a soluble acid and a slightly soluble or insoluble base may be precipitated in an insoluble form, unvarying in composition, when the proportion of the base is exactly such as to cause the precipitation of the salt of this composition; but if the proportion of the base is increased the salt will still be precipitated, but its composition will be different, for it now consists of greater quantities of base for the same quantity of acid.

A metal, such as mercury, dissolved in nitric acid, will unite, in the process of oxidation, with quantities of oxygen varying between a maximum and a minimum. We cannot, therefore, maintain with Lavoisier that when a salt is formed by the action of an acid upon a metal, there is a constant relation between the quantity of the metal and the quantity of oxygen which the former takes from the acid in the process of oxidation.

These propositions of Berthollet were first opposed and successfully refuted by S. L. Proust. Having remarked, in 1799, that upon dissolving native carbonate of copper in an acid, and then precipitating the solution by an alkaline carbonate, he obtained a quantity of carbonate of copper equal to that of the native carbonate which had been dissolved, Proust drew from this fact the conclusion that the composition of carbonate of copper is fixed and invariable, whether the salt has been formed in the depths of the earth or artificially by a chemical process. His subsequent researches enabled him to generalise this conclusion; and in speaking of these researches we must specially quote those upon the composition of the two oxides of tin, the sulphides of iron, and sulphide of antimony. In all these compounds the relation in weight between the two elements is constant; and if two simple bodies, by combining in different proportions, are able to form several compounds, as is the case with tin and oxygen, iron and sulphur, it is evident that in every degree of combination the relation in question is invariable.

Proust brought forward these facts, which he had discovered in opposition to those upon which Berthollet took his stand, and showed that the latter allowed a different interpretation. Metallic solutions, where the metal enters into combination with variable quantities of oxygen; salts, which, when precipitated, may contain variable quantities of bases; or oxides of tin and lead, which have been obtained by the calcination of metals in contact with air, and which have fixed variable quantities of oxygen—in no case consist of, or constitute, definite chemical compounds, but are mixtures, in different proportions, of several compounds, all of which possess a fixed composition. The fixity of composition, indeed, seemed to Proust an essential attribute of combinations, a great law of nature—the *pondus naturæ*, justly recognised by Stahl.

This discussion, which is one of the most memorable of which science possesses a record, lasted from 1799 till 1806, and was maintained on both sides with a power of reasoning and a respect for truth and propriety which have never been surpassed. The fullest development of Berthollet's views appeared in his celebrated work entitled 'Essai d'une Statique chimique,' which was published in 1803. The great idea developed in this book is that chemical affinity and astronomical attraction are different manifestations of an identical property of matter, which led the author to regard not only the energy of affinities as producing chemical reactions, but also the influence of the masses.

In a great number of reactions this influence does undoubtedly govern the progress of decomposition or combination; it augments or diminishes the proportion of compounds which are formed or destroyed in a reaction, but it does not govern the proportions in which the elements unite in these compounds. On this latter point Berthollet held a different opinion; he maintained that mass does exercise an influence upon the combining proportions of two bodies when no physical condition is present to determine the separation of a compound in fixed proportions. Thus, when an acid acts upon a base in such a manner as to produce a soluble salt, the point of neutrality undoubtedly corresponds to fixed proportions of combined acid and base; but if an excess of one or other of these elements be added, it also will enter into combination, and, moreover, in variable proportions, till a physical property—cohesion, for example—determines the separation of a compound of fixed proportions. In a great number of chemical combinations, therefore, this fixity in the proportions of elements may be observed; but, in the opinion of Berthollet, they are exceptional cases, to which it would be wrong to ascribe the dignity of a general law.

Proust, on the contrary, maintained the generality of this law. If it is impossible, he says, to make an ounce of nitric acid, an oxide, a sulphide, or a drop of water in other proportions than in those which nature, from all eternity, has assigned to these compounds, we must acknowledge that for chemical combinations there is a sort of 'balance,' which is subject to the immutable laws of nature, and which, even in our laboratories, determines the relation of the elements in these compounds. The latter are of several orders. The most simple are generally formed of two elements—at most of three, very rarely of four. But these compounds of a simple order may combine with each other, so as to form more complex compounds; in other cases they are merely mixed together. In these mixtures the proportion of the elements is naturally subject to variation; in all chemical combinations properly so called it is, on the contrary, fixed.

The opinion of Proust was well founded; it won the day, in spite of the opposition of his powerful antagonist; and we cannot too much admire the persevering energy and discernment displayed by the chemist of Angers in this contest, when he took one by one the arguments of Berthollet, and opposed to the facts collected and arranged by the latter in support of his theory fresh facts and fresh analyses of his own, which, it must be confessed, were not always models of accuracy. The superior intelligence, however, of an accurate and lofty mind saved him from error in the discussion of results, and made up for the insufficiency of the methods of that time.

This great truth of the fixity of chemical proportions was, then, definitely established in the year 1806. But the discussions between Berthollet and Proust, which agitated the scientific world during the first years of this century, only gave an incomplete idea of it, for they dealt solely with the composition of each compound taken individually. The question as to whether sulphide of antimony was a constant compound, and whether this was also the case with the sulphides of iron, the oxides of tin and cobalt, was answered in the affirmative by Proust, in the negative by Berthollet. It is now definitely decided in the affirmative. We must not, however, forget that Proust and Berthollet only attacked the question from one side, for there is another. It is true that this sulphide of antimony, these sulphides of iron, and, in fact, that all sulphides present a fixed composition; and, again, it is equally true that in every metallic oxide the metal and the oxygen unite in invariable proportions. But this is not all. Analysis shows, further, that the relations between quantities of different metals uniting with a fixed weight of sulphur are the same as those between different metals uniting with a fixed weight of oxygen. Independently, therefore, of the fact of fixity, there is the further fact of the proportionality of the combining quantities or weights of bodies; and the case in question is not an exceptional one, but belongs to a whole order of similar facts—is, in short, a law.

We have, in demonstrating this law of proportionality, employed as examples the very compounds which enabled Proust to establish the law of fixity. It may, however, be demonstrated under a more general and striking form.

A is a certain weight of a simple body.

B is a certain weight of another simple body, which is exactly sufficient to form with A the combination A B. The relation $\frac{A}{B}$ is constant.

C is a certain weight of a third simple body, exactly sufficient to form with A the combination A C. The relation $\frac{A}{C}$ is constant.

D is a certain weight of a fourth simple body, exactly sufficient to form with A the combination A D. The relation $\frac{A}{D}$ is constant.

This is Proust's law.

Let us now take the second body B, and form combinations between this body and the third C and the fourth D. Experience shows us that the quantities C and D which combine with A will also combine with B—in other words, that the weights of the bodies B, C, D, which formed definite compounds with A, are unchanged when they combine with each other. From the fact of the existence of compounds A B, A C, A D, we may assume the existence of compounds B C, B D, C D, in which the quantities A, B, C, D, are constant. In short, there exists between all compound bodies formed by the union of two elements such a definite relation of composition that we have only to determine the proportions in which the most widely differing elements unite with one of their number, and we shall also have determined the proportions in which they combine with each other.

This is the law of proportionality, discovered by Richter, who lived at Berlin towards the close of the last century.

For many years another German chemist—C. F. Wenzel—was considered the author of this great discovery. It was attributed to him by Berzelius.[1] M. Dumas also claims it for him,[2] and all chemical treatises fifty years ago quoted him as the precursor of Richter. He was rather the rival of Bergman and Kirwan. The analyses of neutral salts which he published were accurate; but he nowhere mentions the fact of the preservation of neutrality after the double decomposition of the two neutral salts; he admits, on the contrary, that in the phenomenon in question the quantity of the two neutral salts which react upon each other being calculated after their known composition, a certain excess of one of the elements may remain after the decomposition has taken place. This opinion is contrary to facts, and must necessarily have rendered it impossible for the author to discover the law of proportionality. This law was demonstrated a few years later by a much less experienced chemist than Wenzel, who was obscure and diffusive in his productions, but endowed with singular penetration and rare perseverance.

---

[1] The following are the terms in which Berzelius claimed for Wenzel the discovery of the proportionality of quantities of acids and bases which exactly saturate each other:—'He published the result of these experiments in a memoir entitled *Lehre von den Verwandtschaften*, or the *Theory of Affinities*, at Dresden in 1777, and proved, by singularly accurate analyses, that this phenomenon (the preservation of neutrality after the mutual decomposition of two neutral salts) was due to the fact that the quantities of alkalies and earths which saturate a given quantity of the same acid are the same for all acids; so that if we decompose, for example, calcium nitrate by potassium sulphate, the potassium nitrate and the calcium sulphate obtained will preserve their neutrality, because the quantity of potash which saturates a given quantity of nitric acid is to the quantity of lime which saturates the same quantity of nitric acid as the potash is to the lime which neutralises a given quantity of sulphuric acid.'—*Traité de Chimie*, French edition, 1831, t. iv. p. 524.

[2] *Chemical Philosophy*, p. 200. The error concerning the part attributed to Wenzel in the discovery of the law of proportionality has been corrected by several scientific writers—first by Hess (*Journal für praktische Chemie*, t. xxiv. p. 420); then by Schweigger, in the work entitled *Ueber stöchiometrische Reihen im Sinne*

II.

J. D. Richter was preoccupied with the idea of applying mathematics to chemistry, and particularly with that of discovering numerical relations between combining bodies. His efforts in this direction did not meet with success; for, though he was the first to recognise and demonstrate the law of proportionality between the quantities of bases uniting with a given weight of acid, and between the quantities of acids uniting with a given weight of base—a most important and well-established fact—he fell into error in trying to show that these

Richter's, Halle, 1853; lastly by R. A. Smith (*Memoir of J. Dalton, and History of the Atomic Theory up to His Time*, London, 1856).

quantities form numerical series, the terms of which bear to each other a simple ratio.[1] But we need not pay much attention to this point. Let us rather gather from the work of Richter the great truths and fundamental discoveries which demand the grateful recognition of posterity, all the more strongly from the fact that they were neglected and almost ignored by his contemporaries.

Richter founded his researches upon the then well-known fact of the permanence of neutrality in the double decomposition of two neutral salts. Richter found and clearly demonstrated the required explanation of this fact. In the first volume, published in

---

[1] Richter tried to show that the quantities of bases which saturate a given weight of acid represent the terms of an arithmetical progression, and that the quantities of acids which combine with a given weight of base form the terms of a geometrical progression. Thus, for example, he found that 1,000 parts of hydrochloric acid are saturated by 734 of alumina, 858 of magnesia, 1,107 of lime, and by 3,099 of baryta. These numbers form the terms of a series a, $a+b$, $a+3b$, $a+19b$, in which $a=734$ and $b=124{\cdot}5$. Having afterwards discovered the saturating capacity of strontia for hydrochloric acid, he found that this base would occupy the place $a+11b$ in the preceding series, a result which he soon corrected to $a+9b$.

A different but very simple relation exists, in his opinion, between the quantities of acids which saturate a given quantity of base. Thus the quantities of fluoric (hydrofluoric) acid 696·4, muriatic acid 1160·0, sulphuric acid 1630·0, and nitric acid 2290·4, which saturate 1,000 of magnesia, form the first, third, fourth, and fifth terms of geometrical progression—c, cd, cd^3, cd^5, cd^7—the first term of which c is $=696{\cdot}4$, and $d=1{\cdot}1854$. Again, the quantities of carbonic, sebacic, oxalic, formic, succinic, acetic, citric, and tartaric acid necessary to neutralise a given base increase according to a geometrical progression a, ab, ab^2, ab^3. Metallic acids, on the contrary, are subject to another law: the quantities of tungstic, chromic, arsenic, and molybdic acid which saturate a given weight of base constitute the terms of an arithmetic progression.

1792, of his 'Elements of Stoichiometry'[1] he expresses himself as follows:—Let A and B represent the weights or masses of two neutral compounds (salts) which exactly decompose each other; the new bodies will remain neutral: let a represent the mass of an element in A, and b that of an element in B; the masses of the two elements in A will be a, $A-a$, and in B will be b, $B-b$. Before decomposition the ratio of the masses (weights) of the neutral compounds A and B will be

$$\frac{a}{A-a} \text{ and } \frac{b}{B-b}.^{2}$$

After decomposition the masses of the elements in the

All these propositions are founded upon inaccurate data, a fact which doubtless did not escape the notice of some of Richter's contemporaries, and contributed to throw discredit upon his labours. He himself sometimes saw the necessity of correcting some of these errors; but though he gave up a few details, he still held to the numerical laws demonstrated above—the new figures always adapted themselves to it. Thus in 1797 soda changes its place in the series of bases neutralising a given weight of sulphuric acid. Richter now finds that 1,000 parts of this acid are saturated by 672·1 of volatile alkali (instead of 638), by 858·6 of soda (instead of 1,218), and by 1604·6 of potash (instead of 1,606). These numbers increase as the terms $a, a+b, a+5b$, while the original numbers formed the terms of a series $a, a+3b, a+5b$.

These are great imperfections in the work of Richter; but, though we cannot but regret that his memory should be charged with them, they must not cause us to forget the great truths which he had the honour of discovering.

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[1] *Anfangsgründe der Stöchiometrie, oder Messkunst chemischer Elemente.*

[2] We have reversed these fractions, which the author wrote—

$$\frac{A-a}{a} \text{ and } \frac{B-b}{b}.$$

new products will be a, $\mathrm{B}-b$ and b, $\mathrm{A}-a$, and the ratio of these masses will be

$$\frac{a}{\mathrm{B}-b} \text{ and } \frac{b}{\mathrm{A}-a}.$$

If, then, the ratio of the masses (elements) is recognised in the original compounds, the same ratio must be acknowledged in the new compounds.

Richter drew up, in 1793, a table which he termed *series of masses*—the quantities of analogous elements (acids or bases) which combine with a given weight of another element. In another part of the work which we have just quoted he definitely states the following proposition:—The different quantities of bases which form neutral salts with 1,000 parts of anhydrous muriatic acid also form neutral salts with a given weight (1,394 parts) of anhydrous sulphuric acid. It follows, from the formula given above, that if we take a weight A of a muriate (chloride) containing 1,000 parts of acid and a weight $\mathrm{A}-1000$ of base, and a weight B of a sulphate containing 1,394 of sulphuric acid, and $\mathrm{B}-1394$ of a second base, this quantity of the latter base will exactly neutralise 1,000 parts of muriatic acid, while the quantity $\mathrm{A}-1000$ of the first base will exactly neutralise 1,394 parts of sulphuric acid.

If, therefore, we mix the two original salts, the neutral muriate and sulphate, we shall obtain from the double decomposition a new sulphate and a new muriate, which again will be neutral. Richter thus explains the fact of the permanence of neutrality when two neutral salts exchange their bases and acids. He at this time

(1793), and in the same work, gave the first 'series of masses' for the alkaline bases and for the earths—that is to say, the equivalent quantities of bases which saturate a given weight (1,000 parts) of sulphuric, hydrochloric, and nitric acids.

The following is the series:—

	Sulphuric Acid	Muriatic Acid	Nitric Acid
Potash	1,606	2,239	1,143
Soda	1,218	1,699	867
Volatile alkali . .	638	889	453
Baryta	2,224	3,099	1,581
Lime	796	1,107	565
Magnesia . . .	616	858	438
Alumina . . .	526	734	374

Although these figures are far from correct, they allow the deduction of the law of proportionality, with which the name of Richter is justly connected. He afterwards completed and corrected them. Having ascertained the quantities of lime and potash which neutralise 1,000 parts of fluoric (hydrofluoric) acid, he proved that these quantities are very nearly proportional to those which neutralise 1,000 parts of muriatic acid. On this point he affirms that 'the masses of alkalies or alkaline earths, when they maintain neutrality with a given mass of either of the three other volatile acids,[1] will always bear to each other the same ratio.' The idea is correct, though the form of expression is not happy. Richter, indeed, generally failed in the latter respect. Thus he endeavours to generalise the law he has discovered by terming the substance (the acid, for example) which enters into combination with a series of analogous substances (bases) the *determining element*, and the latter the *elements determined*.

---

[1] Sulphuric, muriatic, and nitric acids.

Let P represent the mass of a determining element, the masses of 'its' elements determined being a, b, c, d, e, &c.; Q the mass of another determining element, α, β, γ, δ, ε, &c., being the masses of 'its' elements determined; so that a and α, b and β, c and γ, d and δ, and e and ε shall represent the same elements; and, further, that $P+a$ and $Q+\beta$, $P+b$ and $Q+\gamma$, $P+c$ and $Q+\alpha$, &c., are decomposed by double affinity, so that the new products will remain neutral. We shall observe that the masses a, b, c, d, e, &c., bear to each other the same ratio as the masses α, β, γ, δ, ε, &c. Such is the discovery of Richter as he himself published it in 1795 in the fourth part of his 'Mittheilungen über die neueren Gegenstände der Chemie.'

This is not all. We owe to his penetration another important discovery which is closely connected with the one we have just mentioned.

We shall now direct our attention to metallic salts properly so called. When two of these salts are decomposed by double affinity—that is to say, when they exchange their acids and bases—the metal of the one finds in the other exactly the quantity of oxygen necessary to keep it dissolved in the acid; in other words, the quantities of different metals necessary for the formation of neutral salts absorb the same quantity of oxygen when they dissolve in a given weight of acid. This proposition, which is, moreover, very accurate, assumed a clearer form when Lavoisier some time afterwards worded it thus :—The different quantities of oxides which combine with a given weight of acid contain the same quantity of oxygen. Richter followed up these investigations with great success. He admits that the ratios in which oxygen combines with other bodies, particularly metals, are perfectly fixed, and that the quantity of oxygen fixed by a metal during solution in an acid is not always the same as that which it absorbs when heated in contact with air. He is thus led to distinguish several degrees of oxidation, notably in the case of iron and mercury. The latter forms two oxides capable of producing salts. Each of these salts presents a perfectly fixed composition, and passes without alteration of composition by double exchange from one salt to another. These researches date from the close of the last century, and it seems as if, from the manner in which they were conceived and expressed, the influence of Lavoisier had made itself felt, unknown to the author and in spite of his opposition to the doctrines of the reformer. The very fact of this opposition seems, in a great measure, to have been the cause of the discredit thrown upon the labours of Richter; his time was not yet come; other topics created more interest; and in Germany, as also in France and England, men's minds were engrossed by the influx of new ideas.

There is some difficulty in harmonising the signification and even the publication of Richter's great discoveries with the phlogistic theories which he maintained, and which apparently influenced his observations.

Strictly speaking, we can understand that he could have regarded acids as undecomposable bodies, for he only considered their relative weights, which are independent of their constitution. But when we turn to his opinions upon the nature of oxides, upon the fixity of their composition, upon the equality of the weights of oxygen absorbed by metals when dissolved in equivalent quantities of acid, how can we reconcile these correct and simple notions with the erroneous conception of phlogiston? It must be confessed that Richter adapted all this to his theory. He held that the metallic calces or oxides were formed by the combination of metals with oxygen, causing a loss of imponderable phlogiston and most curious contortion of the phlogistic theory. Had he but said heat instead of phlogiston, he would have been quite right. We may, therefore, absolve Richter on this head; but his contemporaries were more severe, and he himself confesses that in 1799 he was declared by the partisans of antiphlogistic doctrines to have taken leave of his senses.

The profound but perplexed author of the great discovery in question—the proportionality which exists between the weights of elements in chemical combinations—was fortunate in having an intelligent and ingenious commentator. G. E. Fischer published in 1802 a German translation of Berthollet's 'Researches upon Affinity,' and further endeavoured in this work to explain and simplify the deductions which Richter made from the fact of the permanence of neutrality after the decomposition of two neutral salts. He succeeded, and simplified the demonstration of the law of proportionality in the following manner :—Richter had given a series of neutralisation for each acid and each base; he had determined the quantities of bases which saturate 1,000 parts of sulphuric acid, 1,000 parts of nitric acid, and 1,000 parts of hydrochloric acid; and then, again, he had indicated the quantities of acids which would saturate 1,000 parts of each base. Though admitting that the quantities of acids and the quantities of bases composing these series are proportional, he uselessly multiplied the number of the latter. Fischer saw that they might be reduced to one by giving the ratio which the quantities of acids and bases contained in the series bear to one number, 1,000 parts of sulphuric acid. In fact, he drew up the first table of chemical equivalents as follows :—

Bases.		*Acids.*	
Alumina	525	Fluoric acid	427
Magnesia	415	Carbonic „	577
Ammonia	572	Sebacic „	706
Lime	793	Muriatic „	712
Soda	859	Oxalic „	755
Strontia	1,329	Phosphoric „	979
Potash	1,605	Formic „	988
Baryta	2,222	Sulphuric „	1,000
		Succinic „	1,209
		Nitric „	1,405
		Acetic „	1,480
		Citric „	1,583
		Tartaric „	1,694

The figures in these two columns represent equivalent quantities of acids and bases. To neutralise a given base of the first series with a given acid of the second series, we must take of that base and that acid the quantity indicated by the accompanying figures.

The ratios of neutrality between the bases and acids are expressed by these numbers, and the table demonstrates in a striking and convenient form the composition of a large number of neutral salts.

The foregoing table forms part of a note which was inserted by Fischer in Berthollet's 'Chemical Statics.'[1] It is to his translator that the latter owed his acquaintance with the researches of Richter. He had treated of the same subject in a chapter of the 'Statics' entitled 'Acidity and Alkalinity,' and had mentioned the opinion of Guyton de Morveau upon the inference which may be drawn from the permanence of neutrality after the decomposition of certain neutral salts, so as to calculate beforehand or control the composition of the salts produced. Both chemists, however, acknowledged that Richter had anticipated them in this direction Berthollet expresses himself on this point as follows:—'The preceding observations appear to me necessarily to lead to the conclusion that in my researches I have only hinted at the laws of affinity, but that Richter has positively established the fact that the different acids follow proportions corresponding with the different alkaline bases in order to produce neutrality. This fact may be of the greatest utility in verifying the experiments which have been made upon the proportions of the elements of salts, and even to determine those which have not yet been decided by experiment, and so furnish the surest and easiest method of accomplishing this object, so important to chemistry.'

Thus Berthollet admitted the law of proportionality, discovered by Richter, though at the same time he questioned the fixity of certain chemical combinations. He considers it possible for neutral salts, precipitated in an insoluble state or separated as crystals from their solutions, to exist in physical conditions compatible, according to him, with a fixed composition.

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[1] Vol. i. p. 134, 1802.

As we remarked above, we owe to Richter another important discovery. He observed that the quantities of different metals which dissolve in a given weight of acids also combine with the same weight of oxygen. This discovery met with no recognition, and was made afresh by Gay-Lussac in 1808. It was the same with the following fact, which Richter established: that certain metals, such as iron and mercury, have the power of combining with oxygen in several proportions, so as to form two degrees of oxidation. Proust rediscovered this fact, and laid great stress upon it in his discussion with Berthollet, but he failed to observe that the quantities of oxygen contained in the different oxides of a given metal increase in a very simple ratio.[1]

We find, therefore, that at the close of the last and the commencement of the present century a number of definite facts were discovered concerning the composition of salts and chemical compounds in general, but that these facts were isolated and without connection. Their deep signification escaped the observation of chemists, and the theoretical link which unites them was entirely unknown. It was reserved for an English chemist to complete them by a discovery of the first order and to arrange them by an hypothesis both simple and fruitful.

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[1] Proust admitted that 1,000 parts of copper combine with $17\frac{2}{3}$ to 18 parts of oxygen to form the first or sub-oxide of copper, and with 25 parts of oxygen to form the second or black oxide. The correct numbers are 12·6 and 25·2. Had the analyses of the two oxides been more correct, Proust might have recognised the law of multiple proportions.

III.

In 1802 John Dalton, at that time a professor in Manchester, was investigating the action of air upon binoxide of nitrogen in the presence of water. He observed that the oxygen contained in 100 volumes of air united with either 36 or 72 volumes of binoxide of nitrogen, leaving a residue of pure nitrogen gas above the water. He concluded from this fact that oxygen combined with a certain quantity of binoxide of nitrogen or with double that quantity, but not with any intermediary quantities, nitric acid being formed in the first instance, nitrous acid in the second. In this observation we have the germ of the law of multiple proportions, although it was not as yet formally stated in the memoir in question.[1] It was announced at the same time as the atomic theory, by which it is theoretically explained, in a communication by Dalton to Thomson in August 1804. He was then studying the composition of marsh gas, and observed that for the same quantity of carbon this gas contains a quantity of hydrogen exactly double that which is contained in bicarburetted hydrogen. We learn further from Thomson[1] that the foundations of Dalton's theory were derived from his researches into the composition of combinations of oxygen and nitrogen, and that, in fact, the observation mentioned above upon the absorption of oxygen by binoxide of nitrogen first gave him an insight into the composition of those combinations. Beyond this it is difficult to affix any precise date to the discoveries of Dalton, or at least to trace the logical sequence and successive evolution of his ideas, and to separate the origin of the law of multiple proportions from the origin of the conception of the atomic theory.

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[1] *Memoirs of the Literary and Philosophical Society of Manchester*, vol. v. p. 535

In fact, in a memoir upon the absorption of gases by water, read in October 1803 before the Literary and Philosophical Society of Manchester, Dalton attributed—erroneously, moreover—the unequal solubility of the different gases to the circumstance that their ultimate particles are not equal in weight, and that the elementary atoms of which they are formed are not equal in number.

In this memoir he remarked that he had for some time been occupied with an endeavour to determine the relative weights of the ultimate particles of bodies—a new and, as he says, most important consideration. Without laying any special stress upon the development of these ideas, he gives in his memoir the first table of atomic weights as follows :—

Hydrogen	1
Oxygen	5·5
Nitrogen	4·2

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[1] *History of Chemistry*, vol. ii. p. 289. London, 1831.

Phosphorus	7·2
Sulphur	14·4
Carbon	4·3
Water	6·5
Ammonia	5·2
Protoxide of nitrogen	13·7
Binoxide of nitrogen	9·3
Nitric acid	15·2
Phosphoretted hydrogen	8·2
Sulphuretted hydrogen	15·4
Sulphurous acid	19·9
Sulphuric acid	25·4
Carbonic oxide	9 8
Carbonic acid	15·3
Marsh gas	6·3
Olefiant gas	5·3
Ether	9·6
Alcohol	15·1

Let us first remark that not only the law of multiple proportions but also the atomic theory are clearly contained in this table. This result is evident from the following data:—

4·3	of carbon	are combined with	1	of hydrogen in	5·3 of olefiant gas.
4·3	,,	,,	2	,,	6·3 of marsh gas.
4·3	,,	,,	5·5	of oxygen in	9·8 of carbonic oxide.
4 3	,,	,,	2 × 5·5	,,	15·3 of carbonic acid.
14·4	of sulphur	,,	5·5	,,	19·9 of sulphurous acid.
14·4	,,	,,	2 × 5·5	,,	25·4 of sulphuric acid.
4·2	of nitrogen	,,	5·5	,,	9·7 (9·3) of binoxide of nitrogen.
4·2	,,	,,	2 × 5·5	,,	15·2 of nitric acid.
2 × 4·2	,,	,,	5·5	,,	13·9 (13·7) of protoxide of nitrogen.

It is true that these figures are very inaccurate, but the inaccuracy of the numerical data cannot conceal or diminish the grandeur and simplicity of the theoretical conception.

Dalton here regards chemical combinations as formed by the addition of elementary atoms, the relative weights of which he endeavours to determine, referring these weights to one of the elements—hydrogen—as unity. When two bodies combine in several proportions, the combination can only be effected by the addition of entire atoms: it follows, therefore, that, the proportion of the one body remaining constant, the proportions of the second must be exact multiples of each other. It is, then, clear that as early as the year 1803 or 1804 Dalton had, if not formally stated, at least conceived and implicitly admitted the law of multiple proportions, as well as the atomic hypothesis, which may almost be regarded as the theoretical representation of the fact of fixed and of multiple proportions. A few years afterwards he gave his opinion upon this subject in the following terms: [1]—

'In all chemical researches great importance has with justice been attached to the determination of the relations according to which elements unite to form compound bodies; but, unfortunately, the subject has not been followed up, though the consideration of these relations might have led to important consequences concerning the relative weights of the smallest particles, or atoms, of bodies.'

From the year 1804 the atomic theory inspired all Dalton's labours and influenced all his thoughts; he confesses himself the influence which this idea had upon him in his representation of the constitution of marsh gas, which he was studying in 1804. It occasioned the discovery of multiple proportions, and afterwards furnished, by a happy reaction, a solid foundation for the atomic hypothesis. The latter was not, however, new to the epoch of Dalton. Not to speak of the atomists of the seventeenth century, who had revived, though at the same time distorted, the ancient conception of the Greek philosophers, we must not forget that Van Helmont, N. Lemery, and Boerhaave had mentioned the indivisible particles of bodies, and had termed them 'atoms,' and that Boyle had tried to explain the differences between chemical attractions by the inequality of the 'massulæ' or particles.

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[1] *A New System of Chemical Philosophy*, part i. London, 1808.

This was a correct conception: the ultimate particles of bodies differ in their relative weight, and doubtless in their size and form. In 1790 Higgins opposed this hypothesis, erroneously attributing the same weight to atoms which combine in very simple proportions to form compound bodies. Thus Higgins admitted that one ponderable part of sulphur in sulphurous acid is combined with one ponderable part of oxygen, and in sulphuric acid with two ponderable parts of oxygen, and that these compounds may be represented as consisting, the first of one atom of sulphur with one atom of oxygen, the second of one atom of sulphur with two atoms of oxygen, the atoms of these two elements being, moreover, of the same weight. He consequently represented these compounds as formed by the union of particles or atoms, of the same weight, but united in different proportions—one of nitrogen for two of oxygen in binoxide of nitrogen, and one of nitrogen for five of oxygen in nitric acid.

This is all perfectly clear, but the starting point is wrong. The proportions in which bodies combine do not represent equal weights. This was an established fact in the time of Higgins, and he is obliged to acknowledge it in the case of water, the two elements of which unite in very unequal proportions; if therefore, as he admitted, water was composed of one atom of oxygen and one atom of hydrogen the atoms of these two elements could not be equal in weight. Higgins's conception was, therefore, spoilt by errors and contradictions, and it is useless to attempt to represent him as one of the authors of the modern atomic theory. This honour belongs to Dalton alone. This great man began to consolidate and publish his views about the year 1808. Thomson and Wollaston were at that time developing the law of multiple proportions. In a memoir upon oxalic acid Thomson showed that the acid oxalate of potash contains twice as much acid as the neutral oxalate. Wollaston demonstrated that this law applies to the quantities of bases and acids contained in basic and acid salts, these quantities bearing a simple ratio to each other. He showed that this is the case in the compounds of potash and soda with carbonic and sulphuric acids, and especially in the compounds of oxalic acid with potash. He points out that the latter are three in number, and that the quantities of acid which they contain for the same proportion of base increase as the numbers 1, 2, 4.

At this time Dalton himself published his theory in the first part of his 'New System of Chemical Philosophy,' which appeared in 1808. The new and comprehensive idea of representing compound bodies as formed of groups of atoms, fixed in number, and possessing different, but at the same time fixed, relative weights, might, it seemed to him, be graphically expressed by the adoption of symbols representing these atoms, and grouped in such a manner as to indicate the composition of bodies. Each atom was represented by a small circle bearing a particular sign.

This is the origin of chemical notation, the language of symbols and numbers, which is clearer and more concise than that of words, and has since been a great instrument of progress in science and a great assistance in instruction. In the work mentioned above Dalton gives a new table of atomic weights, more complete and less incorrect than the preceding one. We give a few of these atomic weights.

	Dalton's Atomic Weights.	Correct Numbers.
Hydrogen	1	1
Nitrogen	5	4·66
Carbon	5	6
Oxygen	7	8
Phosphorus	9	10·3
Sulphur	13	16
Iron	38	28
Zinc	56	65·2
Copper	56	64·5
Lead	95	104
Silver	100	108
Platinum	100	98·5
Gold	140	197
Mercury	167	200

We have omitted in this table the atomic weights of the alkalies and earths which are still placed among the elements, though Dalton must have already been acquainted with the great discovery of H. Davy upon the nature of the alkalies. The above figures give, however, a sufficiently good idea of the accuracy, or rather the inaccuracy, to which Dalton had attained in his own determinations, or in the discussion of those of others. At the same time they show us the exact sense in which we must regard these atomic weights. They are not, properly speaking, atomic weights in the sense which we now ascribe to the term; they are proportional numbers referred to unity, which represents the weight of hydrogen in hydrogen compounds. This may be seen from the following table, in which, for the sake of brevity, we have employed the symbols in use at the present day:—

	Atomic Weights.
Water contains 1 at. H, which weighs 1, and 1 at. O, which weighs 7	8
Sulphuretted hydrogen contains 1 at. H, which weighs 1, and 1 at. S, which weighs 13	14
Ammonia contains 1 at. H, which weighs 1, and 1 at. N, which weighs 5	6
Olefiant gas contains 1 at. H, which weighs 1, and 1 at. C, which weighs 5	6
Marsh gas contains 2 at. H, which weigh 2, and 1 at. C, which weighs 5	7
Carbon protoxide contains 1 at. C, which weighs 5, and 1 at. O, which weighs 7	12
Carbonic acid contains 1 at. C, which weighs 5, and 2 at. O, which weigh 14	19
Protoxide of nitrogen contains 2 at. N, which weigh 10, and 1 at. O, which weighs 7	17

	Atomic Weights.
Binoxide of nitrogen contains 1 at. N, which weighs 5, and 1 at. O, which weighs 7	12
Nitrous acid contains 2 at. N, which weigh 10, and 3 at. O, which weigh 21	31
Nitric acid contains 1 at. N, which weighs 5, and 2 at. O, which weigh 21	19

We see that the atomic weights of oxygen, sulphur, nitrogen, carbon, and phosphorus are deduced from the composition of their combinations with hydrogen, in which the existence is admitted of one atom of hydrogen combined with one atom of another body; and when there are two combinations with hydrogen, as is the case with carbon, the atomic weight is determined from that containing the least quantity of hydrogen. Thus the atomic weight of carbon is the quantity of carbon combined with 1 of hydrogen in olefiant gas. In marsh gas this quantity of carbon is combined with 2 of hydrogen.

Such are the principles by which Dalton was guided in the determination of atomic weights, as they were conceived by him in 1808, and in the notation which was deduced from them. These principles are clearly demonstrated in the following table, which expresses the atomic constitution of the compounds mentioned above; the formulæ are analogous to those now in use:—

Dalton's Notation (1808).

Atomic (Molecular) Weight.		Formulæ.
8	of water are represented by	HO
14	„ sulphuretted hydrogen	HS
6	„ ammonia	HN
6	„ olefiant gas	HC

Dalton's Notation (1808)—continued.

Atomic (Molecular) Weight.		Formulæ.
7	of marsh gas	H_2C
12	„ carbon protoxide	CO
19	„ carbonic acid	CO_2
17	„ protoxide of nitrogen	N_2O
12	„ binoxide of nitrogen	NO
31	„ nitrous acid	N_2O_3
19	„ nitric acid	NO_2

CHAPTER II.

LAW OF VOLUMES.

GAY-LUSSAC—AVOGADRO AND AMPÈRE—BERZELIUS.

I.

The atomic weights established by Dalton were really proportional numbers; they represented the proportion in which bodies combine, expressed by the relative weights of their ultimate particles. The atoms of simple bodies are equivalent to each other. We may, therefore, consider the terms *atomic weights*, *proportional numbers*, and *equivalents* as at this time synonymous. We owe the last term to Wollaston; H. Davy preferred the expression 'proportional numbers.'

The atomic constitution of bodies follows very naturally from the ideas of Dalton. In binary compounds atoms unite in the ratio of 1 to 1, and in multiple compounds formed by two given elements in the ratio of 1 to 1, 1 to 2, 1 to 3, 2 to 3, &c. This simple conception, which is clearly demonstrated in the table upon the preceding page, had to be modified in accordance with Gay-Lussac's great discovery.

The relations between the combining volumes of gases are very simple, and the volume of the compound formed bears, moreover, a very simple ratio to the sum of the volumes of the combining gases.

This proposition embraces a great number of facts, which present no exceptions and which together constitute a great law of nature, the law, namely, of Gay-Lussac. Suitably interpreted, it has become one of the foundations of chemical science. The following are the facts; the interpretation will be developed presently:—

2 vol. of hydrogen unite with 1 vol. of oxygen to form 2 vol. of aqueous vapour.[1]
2 vol. of nitrogen unite with 1 vol. of oxygen to form 2 vol. of nitrogen protoxide.
1 vol. of nitrogen unites with 1 vol. of oxygen to form 2 vol. of nitrogen dioxide.
1 vol. of nitrogen unites with 2 vol. of oxygen to form 2 vol. of nitrogen peroxide.
1 vol. of chlorine unites with 1 vol. of hydrogen to form 2 vol. of hydrochloric acid gas.
2 vol. of chlorine unite with 1 vol. of oxygen to form 2 vol. of hypochlorous anhydride.
1 vol. of nitrogen unites with 3 vol. of hydrogen to form 2 vol. of ammonia.
2 vol. of carbon protoxide unite with 2 vol. of chlorine to form 2 vol. of phosgene gas.
2 vol. of ethylene unite with 2 vol. of chlorine to form 2 vol. of vapour of ethylene chloride.

Thus it appears that very simple relations exist not only between the volumes of gases entering into combination, but also between these volumes and the volume occupied by the gas or vapour of the compound body. It should be remarked, moreover, that, as far as we know at present, the volumes of the combining gases are always reduced to 2 vol. after combination.[1] Bearing this fact in mind, we may return to our historical account.

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[1] The volumetric composition of water was discovered in 1805 by Gay-Lussac and Humboldt. This observation formed the starting point of Gay-Lussac's discoveries.

Gay-Lussac rendered unexpected assistance to the ideas of Dalton. The fixed relations which are admitted between the weights of elements entering into combination, the simple relations which exist between the weights of a given element in the multiple combinations of that element, are again encountered when the combining volumes of gases are considered. Connecting these two orders of facts, and following up the interpretation which Dalton gave of the former, may we not conclude that the relative weights of the gaseous volumes entering into combination exactly represent the relative weights of the atoms—in other words, that there exists a simple relation between the specific gravities of elementary gases and their atomic weights? Gay-Lussac perceived this simple relation, and Berzelius defined it a few years afterwards; but Dalton refused to accept it, ignoring and repudiating the solid support which the great French chemist gave to his ideas.

In fact, the relation which exists between the densities of gases and their atomic weights is not so simple as we should at first sight be led to expect, and as for a long time it was thought to be.

It is a difficulty which will soon be apparent, and which has only quite recently been overcome, after sixty years of investigation and labour. Nevertheless the theoretical conception which embraces the two orders of phenomena in question, and which establishes a link between fixed and multiple chemical proportions and the law which regulates the combinations of gaseous volumes, was accurately formulated in 1813 by the Italian chemist Amedeo Avogadro.

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[1] This applies particularly to the first seven cases, in which the volumetric relations are as simple as possible, and cannot be reduced. The two last cases will be discussed presently.

Starting from the discoveries of Gay-Lussac, Avogadro arrived at the conclusion that there exists a simple relation between the volumes of gases and the number of elementary or compound molecules which they contain. The most simple and at the same time the most probable hypothesis which can be brought forward upon this point is, he says, to admit that all gases contain in a given volume the same number of integral molecules.[1] These molecules must, therefore, be equidistant from each other in different gases, and placed at distances which, in relation to the dimensions of the molecules, shall be exactly sufficient to neutralise their mutual attraction. This hypothesis, according to Avogadro, is the only one which gives a satisfactory explanation of the fact of the simplicity of relations between the volumes of gases entering into combination. The following result of this hypothesis is important: if it is true that equal volumes of gases contain the same number of molecules, the relative weights—that is to say, the densities of equal volumes—ought to represent the relative weights of the molecules. Thus the molecular weights of hydrogen, oxygen, and nitrogen will be expressed by the ratio of their densities —i.e. 1, 15, 13.[1] But in considering the molecular weights of compound bodies we encounter a difficulty, which arises from the difference of contraction experienced by gases in the act of combination. Supposing water to be formed by the union of two volumes of hydrogen and one volume of oxygen contracted to one volume, it is clear that the weight of this single volume, compared with that of one volume of hydrogen, would be 17 (15+2);[2] or again, supposing one volume of ammonia were formed by the contraction of three volumes of hydrogen and one volume of nitrogen, the weight of this volume of ammonia must be 16. Now, experiment proves that the densities of aqueous vapour and of ammonia are half the above numbers —namely, 8·5 and 8—a result which agrees with the fact that two volumes of hydrogen and one volume of oxygen are condensed into two volumes of aqueous vapour, and, on the other hand, that three volumes of hydrogen and one volume of nitrogen are condensed into two volumes of ammonia. Since one volume of aqueous vapour contains only one volume of hydrogen and ½ volume of oxygen, a molecule of water can only be formed of one molecule of hydrogen and ½ molecule of oxygen; and, for the same reason, one molecule of ammonia must be formed of 1½ molecule of hydrogen and ½ molecule of nitrogen, and a molecule of hydrochloric acid gas of ½ molecule of hydrogen and ½ molecule of chlorine. It follows that the matter contained in the unit of volume of the elementary gases does not represent the ultimate particles which exist in certain combinations of these gases, for the matter contained in one volume of oxygen, nitrogen, hydrogen, and chlorine must be halved in order to form the quantity of water, ammonia, and hydrochloric acid gas contained in one volume of these compounds. This is the difficulty which strikes us, a difficulty which, according to Avogadro, is easily solved by supposing that the *integral molecules*, an equal number of which are contained in the gases or vapours of elementary bodies, are themselves composed of a certain number of *elementary molecules* of the same kind, just as the *integral molecules* of compound gases and vapours are formed of a certain number of *elementary molecules* of different kinds.

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[1] *Journal de Physique*, vol. xxxiii. p. 58.

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[1] The correct numbers are 1, 16, 14.

[2] These numbers are those of Avogadro.

This is a fundamental idea, and at that time was quite new. Whilst Dalton had only distinguished one kind of ultimate particles—atoms—Avogadro admits the existence of two kinds—an important distinction, which has been established by the progress of science. Avogadro's elementary molecules are *atoms*, while the integral molecules, which are equidistant from each other in gaseous bodies, which are set in motion by heat and excited by affinity, are what we at the present time call *molecules*.

Ideas similar to those of the Italian chemist were published in 1814 by Ampère,[1] who established a distinction between *particles* and *molecules*. The particle, he says, 'is a collection of a definitive number of molecules in a definite situation, occupying a space incomparably greater than that of the volume of the molecules.' And he adds, 'When bodies pass into the gaseous state, their several particles are separated, by the expansive force of heat, to much greater distances from each other than when the forces of cohesion or attraction exercise an appreciable influence, so that these distances depend entirely upon the heat to which the gas is subjected, and that, under equal pressure and temperature, the particles of all gases, whether simple or compound, are equidistant from each other. The number of particles is, on this supposition, proportional to the volume of the gases.' This passage is so remarkable that we have quoted it word for word. But, as a natural consequence of Ampère's proposition, it follows that, the distances between the gaseous particles being the same, and depending solely upon pressure and temperature, the same variations of pressure and temperature should produce the same change of volume in the gases.

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[1] A letter from M. Ampère to M. le Comte Berthollet upon the determination of the proportions in which bodies combine, from the respective number and arrangement of the molecules of which their integral molecules are composed. (*Annales de Chimie*, vol. xc. p. 43.)

This, as we know, is actually the case, and this great physical fact of the sensible equality of the expansion of gaseous volumes follows as the result of the principle propounded by Avogadro and Ampère—namely, the equality of the number of particles contained in equal volumes of gases and the equality of the distances by which they are separated. Neither of them laid any stress upon this result, which clearly supported their hypothesis.

Ampère clearly alludes to it in the passage quoted above, but he only adds that if the hypothesis which he has offered 'agrees with the established results of experiment, and if such results can be deduced from it as will be confirmed by subsequent experiments, it may acquire a degree of probability approaching to what in physics is termed *certainty*.'

Thus, equal volumes of gases and vapours contain the same number of particles, and the latter are formed of groups of molecules. This, in other words, is the conception of Ampère. From geometrical considerations Ampère was led to conclude that each particle consists of four molecules.

'In accordance with this idea,' he says, 'each particle should be regarded as a collection of a definite number of molecules in a definite position, occupying a space incomparably greater than that of the volume of the molecules; and, in order that this space may be of three comparable dimensions, one particle must comprise at least four molecules. In order to express the respective position of the molecules in a particle, we must conceive, by means of the centre of gravity of these molecules, to which we may suppose them to be reduced, planes so placed as to leave on the same side all the molecules which are outside each plane. Supposing that no molecule should be contained in the space included between these planes, this space will be a polyhedron, of which each molecule will occupy an angular point.

If the particles of oxygen, nitrogen, and hydrogen are composed of four molecules, it would follow, according to Ampère, that those of nitrogen dioxide are composed of four molecules—namely, two of oxygen and two of nitrogen—and those of nitrogen protoxide of six molecules—namely, four of nitrogen and two of oxygen.

Thus when gases combine together the molecules contained in the unit of volume of either of the combining gases, and which form its particle, are not always contained integrally in the unit of volume of the compound gas. These molecules may be grouped or separated in forming a particle of the compound gases. Let us translate this idea of Ampère's into the language of formulæ, confining ourselves to the examples quoted above.

The unit of volume of gas contains—

Oxygen	O_4
Hydrogen	H_4
Nitrogen	N_4
Water	H_4O_2
Nitrogen protoxide	N_4O_2
Nitrogen dioxide	N_2O_2
Ammonia	N_2H_6

The analogy will at once be seen between this conception and that which is generally adopted at the present day, and which is expressed by the following formulæ:—

Two volumes of gas contain—

Oxygen	O_2
Hydrogen	H_2
Nitrogen	N_2
Water	H_2O
Nitrogen protoxide	N_2O
Nitrogen dioxide	NO
Ammonia	NH_2

For the first time gases are compared under the same volume, and the matter contained in equal volumes represents the magnitude of the molecules, which is a most essential point. The integral molecules of Avogadro and the particles of Ampère are, in fact, the material parts contained in the unit of volume. These integral molecules, or particles, may be subdivided into elementary molecules, or simply into molecules; and Ampère, from geometrical considerations, ingeniously, though uselessly, multiplies the number of the latter. Both for the first time introduce into science the distinction between two kinds of ultimate particles, and admit that the number of integral molecules or particles is proportional to the gaseous volume.

We now give a more simple form to the same ideas by admitting that gases (and all other bodies) are formed of molecules and atoms; and, in order to avoid the subdivision of molecules referred to one volume, we find it more convenient to refer them to two volumes, assigning the term *molecule* to the matter contained in two volumes. When for an elementary gas this molecule, as is often the case, consists of two atoms, the atom represents the matter contained in one volume; but the general rule is that *equal volumes of gases and vapours contain the same number of molecules, and consequently that the relative weights of these molecules are proportional to the densities.* This is the law, or, if we prefer it, the hypothesis, of Avogadro and Ampère, for we must acknowledge that a hypothesis here becomes mingled with the interpretation of positive facts; but the hypothesis seems to be legitimate, and will be justified presently. Chemists long ignored its import. Another conception was soon substituted for it, which acquired an important place in science, without, however, gaining general consent, though supported by the authority of a great name—that of Berzelius.

II.

In 1813 Berzelius conceived the idea that, in order to represent the composition of bodies, we must take into consideration the relative volumes in which simple gases combine to form compound gases. He developed this idea in a memoir upon the nature of hydrogen. It is well known, he says, that one volume of a gaseous body combines with one, two, or three volumes of another gaseous body; we have only to determine, therefore, the weights of these volumes to know the relative weights according to which the gases combine with one another. It is obvious that the numbers thus obtained are similar to the atomic weights of Dalton, without, however, being identical. Again, though declaring himself a partisan of the atomic hypothesis, Berzelius held that it was better to keep to the theory of volumes, as having the advantage of being founded on well-established facts. In order to express the composition of bodies by weight from this point of view, it is only necessary to find:—firstly, the number of elementary volumes which unite to form a compound body; secondly, the relative weights of these volumes—that is to say, the densities of the elements in the gaseous state. Hence the importance of the determination of gaseous densities. In 1814 Berzelius worked out a number of these densities, referring them to that of oxygen, which he took as 100.

Thus, the weight of an 'elementary volume' of oxygen being 100,
that of an elementary volume of hydrogen will be 6·218,
that of an elementary volume of nitrogen 88·6,
that of an elementary volume of chlorine 221·4.[1]

These weights express the quantities of the bodies which enter into combination. In a great number of cases there are many difficulties in the way of the determination, which can only be made in an indirect manner. In fact, at this period Berzelius was only acquainted with two simple gases of which he could obtain the density—oxygen, namely, and hydrogen. He at that time regarded nitrogen as a body composed of nitrogen and oxygen, and was not as yet converted to Davy's opinion concerning the simple nature of chlorine.

It would, therefore, be only in a very small number of cases that the weight of 'elementary volumes' could be directly proved by experiment, and to determine the weight of non-gaseous simple bodies we should be forced to have recourse to hypotheses upon the composition by volumes of non-gaseous elements. Let us take a few

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[1] We can judge of the accuracy of these numbers by referring them to 6·218 of hydrogen taken as unity. They then bear the following ratios to each other:—

		Correct Numbers.
Hydrogen	1	1
Oxygen	16·08	16
Nitrogen	14·45	14
Chlorine	36·11	35·5

examples. What is the weight of an 'elementary volume' of carbon? We know that carbonic acid gas contains its own volume of oxygen. But do the two volumes of carbonic acid gas, which contain two volumes of oxygen, contain one volume or two volumes of carbon vapour? In the first case the three volumes, two of oxygen and one of carbon vapour, are reduced to two from the effect of combination, a condensation similar to that of water; in the second the condensation is one-half. Thus, on the first hypothesis, it is evident that the weight of the 'elementary volume' of carbon is twice that which is attributed to it in the second. Referred to oxygen as 100, the weight of the 'elementary volume' of carbon is 75·1 in the first case and 37·55 in the second; and the corresponding formulæ of carbonic acid gas will be CO_2 and C_2O_2. Berzelius adopted the first hypothesis, allowing himself to be guided by analogy. It seemed to him probable that the condensation of the elements of carbonic acid gas was similar to the condensation of the elements of water.

He also at this time admitted that the powerful bases must be composed of two elementary volumes of oxygen and one volume of metal. The composition of the oxides of sodium, potassium, calcium, iron, zinc, and lead was, therefore, represented by the formulæ NaO_2, KO_2, CaO_2, FeO_2, PbO_2, the weights of the elementary volumes of a great number of metals thus assuming a value double that which Berzelius attributed to them later.

The theory of volumes, as it stood at that time, was therefore bristling with hypotheses and full of uncertainties. And yet this conception long held its ground in science, especially in France, where at a certain period it was the fashion to express the composition of bodies in 'volumes,' under the impression that the substitution of volumes for atoms had the advantage of offering a representation more in accordance with facts. But in reality it was not so: the volume occupied by carbon vapour, and the degrees of condensation of the elements of carbonic acid gas, were hypothetical ideas, and these 'elementary volumes' represented the atoms themselves, at least in notation.

Berzelius recognised this fact in 1818. In his essay upon the theory of chemical proportions he modified considerably the views which he had published in 1813. The prevailing idea is no longer that of establishing the system of atomic weights upon the theory of volumes. Though still giving weight to the indications furnished by this theory, he endeavours to reconcile it with what he terms the 'corpuscular theory,' which is founded upon chemical proportions. The indivisible corpuscules, or the ultimate particles of bodies, are designated atoms—the most convenient term, because the one most in use. We might call them particles, molecules, or chemical equivalents, as all these terms appear to be synonymous to Berzelius. The relative weights of these atoms represent chemical proportions. The fixed proportions, which had been recognised for weights, again appeared in gaseous combinations for volumes. Thus the theory of volumes and the atomic or corpuscular theory led to the same results, as far as the ponderable relations of elements in combinations are concerned:

what is called atom in one is called volume in the other. It would seem, therefore, as if we might assimilate the two notions, which indeed is necessary in the case of simple gases. Equal volumes of the latter contain the same number of atoms, under the same conditions of temperature and pressure. Berzelius observes that this law does not apply to compound gases; for, he says, it sometimes happens that a volume of a compound gas contains fewer atoms than an equal volume of a simple gas. Thus one volume of aqueous vapour contains one-half as many atoms (compound atoms, molecules) as one volume of hydrogen.

Such was the manner in which Berzelius, about 1818, expressed the atomic hypothesis, which he founded partly upon chemical proportions and partly upon a peculiar conception of the law of volumes. This conception was not a very happy one. Not to mention the difficulty which he created by applying the same term, atoms, to the ultimate indivisible particles of simple bodies and to the complex molecules of compound bodies, a confusion which had been avoided by Avogadro and Ampère, Berzelius at this time introduced into the language of science a formula which long held its ground, and which must now be considered as erroneous—namely, the proposition that equal volumes of simple gases contain the same number of atoms. We shall presently reconsider this point. We must here draw attention to the influence which the discoveries of Gay-Lussac exercised upon Berzelius in his attempt to bring the atomic hypothesis into harmony with the facts relating to the combination of gases. It is a remarkable fact that neither Dalton nor Gay-Lussac accepted the views of the Swedish chemist. The author of the atomic theory obstinately maintained his first idea of deducing atomic weights solely from the ponderable relations of elements in combinations. Gay-Lussac, again, confined himself to the immediate consequences of his discovery, not without forcing them to some extent, in certain cases, by hypotheses upon the forms of condensation of the combining gaseous elements. He and Berzelius expressed the composition of bodies in volumes, the latter admitting that the relative weights of these volumes represented atoms, Gay-Lussac refusing to consider these weights as anything more than ponderable 'relations,' and inclining rather to the views of Davy. The latter, deviating to an equal extent from the profound conceptions of Dalton, and with the idea of completing them by the discoveries of the French chemist, confined himself strictly to established facts and to the consideration of 'proportional numbers.' After the ingenious but ignored attempts of Avogadro and Ampère, and the unfruitful effort of Berzelius, Dalton's conception would have been sentenced to sterility and oblivion, had it not happened that, at the period of which we are speaking, fresh discoveries and new ideas drew attention to it. We allude to Prout's hypothesis, to the discovery of the law of specific heats, and to the discovery of isomorphism.

CHAPTER III.

PROUT'S HYPOTHESIS—LAW OF SPECIFIC HEATS—ISOMORPHISM.

DULONG AND PETIT—MITSCHERLICH

I.

WE must first return to Prout's hypothesis, not that it is of such great importance from our present point of view, but because it preceded the important discoveries which we shall presently mention.

The anonymous author of a memoir which appeared in 1815[1] upon the relations between the densities of bodies in a gaseous state and the weights of atoms, tried to prove that the densities of oxygen, nitrogen, and chlorine are integral multiples of that of hydrogen, and that the atomic weights of certain elements are similarly integral multiples of that of hydrogen. Amongst these elements we meet with some metals, the atomic weight of which had been determined by the author or by other chemists by the following excellent process: the quantities of metal were determined which, combined with oxygen, formed quantities of oxides capable of neutralising the same quantity of an acid. The results appear in the following table:—

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[1] *Annals of Philosophy*, vol. vii. p. 111.

H = 1
C = 6
N = 14
P = 14
O = 8
S = 16
Cl = 36
I = 124

Ca = 20
Na = 24
Fe = 28
Zn = 32
K = 40
Ba = 70

We will make no remark upon the author's considerations concerning the relations which may be traced between these numbers and those which express the atomic weights of other elements determined with less accuracy. These considerations were obscure and erroneous.

The important point was raised by Prout in 1816, in a work to which he appended his name. 'It is very advisable,' he remarked, 'to adopt the same unit for specific weights and atomic weights, and to take as this unit the weight of one volume of hydrogen. The same numbers will thus give the densities of gases and the atomic weights, or a multiple of these weights. If,' proceeds the author, 'these numbers are whole numbers, the fact under consideration may be interpreted by admitting that hydrogen is the primordial matter which forms the other elements by successive condensations. The figures expressing these condensations—that is to say, the densities—would at the same time give the number of volumes of primordial matter condensed into a single volume of a given element, and the weight of this volume, expressed by a whole number, would represent the atomic weight of the element.'

The determinations of atomic weights, and even those of the densities of gases, were too inaccurate, at the time of which we are speaking, for Prout's hypothesis to be taken into serious consideration. It was a conjecture. It has, as we know, been lately again taken up with great energy by Dumas.[1]

But the accurate determinations of a number of atomic weights by Stas, notably those of chlorine, potassium, sodium, and silver, by confirming or slightly rectifying the results formerly obtained by Marignac, have entirely annihilated the celebrated hypothesis in question. Unsuccessful attempts have been made to revive it, by taking as the unit, not the atomic weight of hydrogen, but the half or the quarter of this weight. There are well-known atomic weights, particularly that of potassium, which are not a multiple of the fraction $\frac{1}{2}$, nor even of $\frac{1}{4}$. If, however, we retained the idea, which is, moreover, striking and profound, of a primordial matter the sub-atoms of which were grouped in different numbers to form the chemical atoms of hydrogen and the various simple bodies, and attributed to these sub-atoms a weight inferior to a quarter of that of hydrogen, assigning to it, for example, $\frac{1}{10}$ of that weight, such an hypothesis would, I say, escape all experimental verification, as the differences which it would then be our object to establish between the atomic weights of the various simple bodies would fall within the limit of errors of observation. Such an hypothesis, though reasonable, ceases to be legitimate, and positive chemistry for the present must abandon this theory of Prout's, this dream of the ancients upon the unity of matter and the compound nature of chemical elements. Does this mean that Prout wrote in vain? By no means. His idea gave rise to valuable work and important discussions, and the example which he set of referring atomic weights to that of hydrogen has been followed, for all chemists have adopted this unit. But at that time, as in our own, Prout's conception produced no argument in favour of the atomic theory, and has exercised no influence upon the development of that theory.

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[1] Dumas made a communication to the Académie des Sciences (January 14, 1878) relative to the atomic weight of silver, discussing the error which had arisen in the determination of this atomic weight, from the property which metallic silver possesses of retaining about $\frac{2}{1000}$ of oxygen, if the latter has not been carefully expelled by heating it in vacuo to 600° C. Dumas maintains the number 108, which he had previously adopted. He remarks that other atomic weights, described as forming exceptions to Prout's hypothesis, might probably be included in the rule, if, in the process of weighing, account were taken of errors similar to those which he had pointed out in the case of silver.

II.

The discovery which we are about to mention is, on the contrary, one of the foundations of the atomic theory. It draws our attention to the relation which exists between the atomic weights and the specific heats of solid elements. In a memoir published in the 'Annales de Chimie' in 1819, Dulong and Petit gave the specific heats of a great number of solid bodies, particularly metals, and remarked that these specific heats were generally inversely proportional to the atomic weights.

Their observations are summed up in the following table:—

	Specific Heats	Relative Weights of Atoms.[1]	Product of the Weight of each Atom multiplied by the corresponding Capacity.
Bismuth . .	0·0288	13·30	0·3830
Lead . .	0·0293	12·95	0·3794
Gold . .	0·0298	12·43	0·3704
Platinum . .	0·0314	11·16	0·3740
Tin . . .	0·0514	7·35	0·3879
Silver . .	0·0557	6·75	0·3759
Zinc. . .	0·0927	4·03	0·3736
Tellurium . .	0·0912	4·03	0·3675
Nickel . .	0·1035	3·69	0·3819
Iron . . .	0·1100	3·392	0·3731
Cobalt . .	0·1498	2·46	0·3685
Sulphur . .	0·1880	2·011	0·3780

This table contained several errors, which were corrected by V. Regnault. Thus the specific heats attributed to tellurium and cobalt were much too high. On the other hand, the atomic weights adopted for these elements were too low.

Disregarding these inaccuracies, which were afterwards corrected, we find that the atomic weights adopted by Dulong and Petit for a large number of metals differ materially from those admitted at the same period by Berzelius. The atomic weights of zinc, iron, nickel, copper, lead, tin, gold, and tellurium were half those which Berzelius attributed to the same metals in their principal oxides, which he then erroneously regarded as dioxides.[1]

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[1] Referred to that of oxygen taken as unity. To compare these numbers with those of Berzelius on p. 62, it will therefore only be necessary to multiply them by 100.

But Dulong and Petit justly remark that the ordinary methods of determining atomic weights by chemical proportions often give a choice between several numbers. 'There is always,' they say, 'something arbitrary in the determinations of the specific weight of elementary molecules (atomic weights); but the uncertainty only rests between two or three numbers, which always bear to each other a very simple ratio.' In this case we should prefer the number which agrees with the law of specific heats. Moreover, the determinations adopted by Dulong and Petit are in accordance with the most firmly established chemical analogies. They only apply to a limited number of simple bodies. 'Still the mere inspection of the numbers obtained points to a relation so remarkable in its simplicity as to be at once recognised as a physical law, susceptible of being generalised and extended to all elementary substances. In fact, the products in question, which express the capacities for heat of atoms of different nature, are so nearly the same for all, that we cannot but attribute these very slight differences to inevitable errors, either in the determination of capacities for heat or in the chemical analyses.' This is quite true; the errors have been corrected, and the exceptions disappeared one by one. But this result was only obtained upon the completion in some points of the great researches commenced in 1840 by V. Regnault upon specific heats, which has only very recently been accomplished. A reform in the system of atomic weights was also necessary, a reform which has taken place slowly and by degrees.

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[1] If we substitute for the double atomic weights of Berzelius those which Dulong and Petit calculated from the specific heats, the following formulæ of Berzelius, ZnO_2, FeO_2, NiO_2, CuO_2, PbO_2, SnO_2, AuO_2, will become ZnO, FeO, NiO, CuO, PbO, SnO, AuO. That the latter are correct Berzelius did not hesitate to acknowledge.

Dulong and Petit recognised the importance of their discovery and did not exaggerate it. They brought to light a great law of nature, which they expressed in the following striking form: 'The atoms of all simple bodies have precisely the same capacity for heat.'[1] This simple statement was of the greatest value to the idea of atoms, which until then rested upon purely chemical considerations, for we here meet with a physical relation between atoms, to which another physical relation was soon added—that, namely, existing between the density of gaseous bodies and the weight of their ultimate particles. In both cases the true formula had been wanting. Dulong and Petit readily discovered it as far as concerns the specific heats of atoms; Berzelius had been less fortunate in his attempt to define the volumes occupied by the latter in gases.

III.

Those were times of great activity, and the fertile discovery which we have just mentioned was soon followed by another, which exercised a manifest influence upon the development of chemical theories. In the month of December 1819 E. Mitscherlich made known the law of isomorphism. The experiments which he was making upon phosphates and arsenates led to the discovery. He first established the fact that these salts resemble each other in composition, if this composition is represented in 'proportions,' phosphoric acid consisting of one proportion of phosphorus and five proportions of oxygen, and arsenic acid of one proportion of arsenic and five proportions of oxygen. This being granted, he observed, further, that the phosphates and arsenates of the same bases, combined with the same quantity of water of crystallisation, possess the same crystalline form. There is, therefore, a correlation between analogy of composition and identity of crystalline form, and it is this which constitutes the discovery. After having established this correlation for salts of the same base formed by two different acids, Mitscherlich observed it again in analogous salts formed by the same acids united with different bases. Thus potash and ammonia on the one hand, and baryta, strontia, and oxide of lead on the other, form, with the same acids, salts analogous in composition and identical in crystalline form. The same identity of forms is found in the carbonates of lime, iron, zinc, and manganese. Mitscherlich was continually adding to his first examples. He showed the identity of the forms of certain sulphates of the magnesian group, which crystallise with the same quantity of water, such as the orthorhombic sulphates of magnesia, zinc, and nickel, and the clinorhombic sulphates of iron and cobalt; and the insignificant errors which crept into these early experiments had at least the advantage of strengthening his conviction. Though he was wrong in affirming that the different forms of sulphate of iron and sulphate of zinc are due to a difference in the quantities of water of crystallisation, he shows that in magnetite and gahnite, which belong to the group of the spinels, the ferrous and zincic oxides form isomorphous combinations with ferric oxide. He prepared iron alum, and showed its isomorphism with ordinary alum, &c.

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[1] Loc. cit., p. 405.

The first definition of the law of isomorphism—that acids of analogous composition and bases of analogous composition, the former with the same base, the latter with the same acid, form salts of identical crystalline form—was not absolutely correct. Mitscherlich himself recognised this subsequently. His discovery of dimorphism revealed the fact that the same substance can crystallise in two different forms. It must, therefore, be also possible for two substances of different nature, but of analogous composition, to crystallise in two different forms.

Facts of this nature, which are exceptions to the law, may be regarded as cases of dimorphism. Mitscherlich also observed that substances which are really isomorphous, which combine and replace each other in the same crystal in every proportion, do not always present a perfect identity of form in isolated crystals, the number and value of the faces and angles being liable to slight variations, though the general form of the crystal remains unchanged.

Such is the discovery of Mitscherlich, and we must now describe the influence which it has exercised upon the development of the atomic theory.

Mitscherlich himself admitted, in his first memoir, that the similarity of properties in compounds of analogous composition and identical form could scarcely be attributed to identity of crystallisation, but that the explanation must be sought for in a primary and mysterious cause, to which must be referred, on the one hand, the fact of combination by fixed 'volumes' (or atoms), and on the other the resemblance of crystals. This primary cause is the atomic structure of the bodies. A similar atomic constitution not only determines the analogy of chemical properties, but also the similarity of physical forms. Mitscherlich thus declares himself a supporter of the ideas of Berzelius upon the constitution of bodies. Following the example of the latter, he expresses it first in 'volumes' and afterwards in atoms. The memoir published in the 'Annales de Chimie et de Physique' of 1821 bears the following significant title: *Upon the identity of crystalline form in various substances, and the relation between this form and the number of elementary atoms in the crystals.* We have already mentioned the restrictions which Mitscherlich was obliged to place upon his original idea. In a work presented to the Stockholm Academy in 1821 he endeavours to give them precision. He there proposes the following questions:—Do compounds formed by different elements with the same number of atoms of one or several other elements possess the same crystalline form? Is identity of crystalline form determined by the *number* of atoms alone, and is this form independent of the chemical nature of the elements?

The replies to these questions are not as absolute as the principle. For the form to remain unchanged in analogous compounds, the elements which replace each other must be mutually isomorphous, as phosphorus and arsenic, or barium, strontium, and lead. Having further observed that certain salts, such as the acid phosphate of soda, can crystallise in different forms, although in the two cases the composition is identical, he attributes this dimorphism to a different arrangement of atoms. Thus the idea that chemical compounds are formed of *atoms*, and that the number and arrangement of these *atoms* exercise an influence upon the physical form of crystals, had evidently made an impression upon him; and the idea is natural, although it is founded upon a comparison some terms of which are wanting. A crystal may be compared to an edifice of definite form. We see its production, growth, and modification. Is it not natural to suppose that this form is due to the accumulation and arrangement of materials, which we call atoms? We are doubtless using figurative language when we compare the molecular edifice, and its construction from these invisible materials, to a monument of human architecture, which rises piece by piece before our eyes. But the necessities of the case are so perfectly answered by this representation that it has passed at once into the language of our general explanations and demonstrations.

However this may be, the atomic theory evidently exercised an influence upon the conception of Mitscherlich and upon the manner in which he stated his discovery. The same number of elementary atoms, he said, combined in the same manner, produce the same crystalline form, and this form is independent of the chemical nature of the atoms and determined solely by their number and arrangement. In spite of necessary restrictions and established exceptions, so great a law could not but act as a solid support to the atomic hypothesis, which had contributed such precise and simple terms for the enunciation of that law.

IV.

But this is not all. Mitscherlich's discovery was the cause of important changes introduced by Berzelius into the system of atomic weights which he had established in 1813, and into the notation of which they are the origin.

He had previously fixed the atomic weight of chromium and iron by attributing to chromic acid the composition CrO_6 and to ferric oxide the composition FeO_3. He now halves the atomic weight of chromium, attributing to chromic acid the formula CrO_3, which makes it agree with anhydrous sulphuric acid, SO_3. Chromium oxide now assumes the composition Cr_2O_3, and, on account of the isomorphism recognised between chromium oxide and ferric oxide (chrome alum and iron alum), the latter oxide becomes Fe_2O_3 and ferrous oxide FeO. Thus was Berzelius forced to abandon an opinion which he had long entertained, one which Dalton, moreover, had never admitted—namely, that a binary compound (that is to say, a combination of two elements) must always contain a *single* atom of one or the other element. The existence of sesquioxides, R_2O_3, was finally admitted.

But the halving of the atomic weights of chromium and iron occasioned other changes.

The chemical analogies and isomorphism of ferrous oxide, FeO, with lime, magnesia, and oxide of zinc made it necessary to attribute to these oxides, and to the strong bases in general, the composition of protoxides, RO, and consequently to halve the atomic weights of a great number of metals, as indeed had already been done by Wollaston, Dulong and Petit (see p. 53). The old formulæ of the sulphates of iron and zinc—

$$FeO_2, 2SO_3 + 14H_2O;\ ZnO_2, 2SO_3 + 14H_2O—$$

became, therefore—

$$FeO, SO_3 + 7H_2O;\ ZnO, SO_3 + 7H_2O.$$

These lower atomic weights agreed, moreover, with the law of specific heats. Berzelius draws attention to this fact, and in future, in the determination of atomic weights, follows three principles which mutually support each other.

1. The law of volumes. He steadily maintains the propositions which he had previously stated—namely, that equal volumes of simple gases contain an equal number of atoms. This proposition was soon to be refuted by the experiments of Dumas and Mitscherlich.

2. The law of Dulong and Petit. This law is subject, it is true, to some exceptions, but is of great assistance in certain cases, where it enables us to control

other determinations. The experiments of Regnault diminished the number of these exceptions, but it is only very recent investigations which have caused their final disappearance.

3. The law of isomorphism. We have seen in the preceding pages the assistance which Berzelius obtained from this law in the determination of atomic weights. We here give the list of atomic weights as given by the great Swedish chemist in 1826, and repeated by him without alteration in 1835.

	Symbols	Atomic Weights referred to Oxygen as 100	Atomic Weights referred to Hydrogen as 1
Oxygen . .	O	100	16·02
Hydrogen . .	H	6·2398	1
Carbon . . .	C	76·44	12·26
Boron . . .	B	136·2	21·82
Phosphorus . .	P	196·14	31·44
Sulphur . .	S	201·17	32·24
Selenium . .	Se	494·58	79·26
Iodine . . .	I	789·75	126·56
Bromine . .	Br	489·75	78·40
Chlorine . .	Cl	221·33	35·48
Fluorine . .	F	116·9	18·74
Nitrogen . .	N	88·52	14·18
Potassium . .	K	489·92	78·52
Sodium . .	Na	290·90	46·62
Lithium . .	L	80·33	12·88
Barium . .	Ba	856·88	137·32
Strontium . .	Sr	547·29	87·70
Calcium . .	Ca	256·02	41·04
Magnesium . .	Mg	158·35	25·38
Yttrium . .	Y	402·51	64·50
Glucinum . .	Gl	331·26	53·08
Aluminium . .	Al	171·17	27·44
Thorium . .	Th	744·90	119·30
Zirconium . .	Zr	420·20	67·34
Silicon . . .	Si	277·31	44·44
Titanium . .	Ti	303·66	48·66
Tantalum . .	Ta	1153·72	184·90
Tungsten .	W	1183·00	189·60

	Symbols	Atomic Weights referred to Oxygen as 100	Atomic Weights referred to Hydrogen as 1
Molybdenum .	Mo	598·52	95·92
Vanadium . .	V	856·89	137·32
Chromium . .	Cr	351·82	56·38
Uranium . .	Ur	2711·36	434·52
Manganese . .	Mn	345·89	55·44
Arsenic . .	As	470·04	75·34
Antimony . .	Sb	806·45	129·24
Tellurium . .	Te	801·76	128·50
Bismuth . .	Bi	886·92	142·14
Zinc . . .	Zn	403·23	64·62
Cadmium . .	Cd	696·77	111·66
Tin . . .	Sn	735·29	117·84
Lead . .	Pb	1294·50	207·46
Cobalt . . .	Co	368·99	59·14
Nickel . . .	Ni	369·68	59·24
Copper . . .	Cu	395·71	63·42
Mercury . .	Hg	1265·82	202·86
Silver . . .	Ag	1351·61	216·60
Gold . . .	Au	1243·01	199·20
Platinum . .	Pt	1233·50	197·70
Palladium . .	Pd	665·90	106·72
Rhodium . .	R	651·39	104·40
Iridium . .	Ir	1233·50	197·68
Osmium . .	Os	1244·49	198·44

The atomic weights of Berzelius are referred to oxygen as 100. Dividing the numbers which express the atomic weights by 6·2398, the atomic weight of hydrogen, we obtain the numbers given in the second column, which are referred to hydrogen taken as unity. The comparison of these numbers with those adopted at the present day, which will be presently given, leads to two important remarks.

In the first place, the system of atomic weights which met with the approval of Berzelius is very similar to that which is adopted at the present day. With the exception of a few modifications which have been added to it,[1] and which do not affect the ruling principles and general features of the whole, we only discover one important difference between the two systems. This difference arises from the atomic weights of the alkaline metals, and of silver, which are twice as great as those which chemical analogies and the law of Dulong and Petit have now forced us to adopt. We shall presently return to this point. Secondly, in examining these numbers of Berzelius, we are struck by their accuracy. Most of these numbers only differ in the decimals from those which we now adopt as true. Such is the result of the enormous amount of labour expended by the Swedish chemist upon the determination of the atomic weights. It is a lasting monument which he has raised to science and his own glory.

Nevertheless Berzelius never succeeded in persuading all chemists to adopt his system of atomic weights. Dissentient voices are always to be heard. Gay-Lussac and Wollaston, following the example of Dalton and Thomson, adhered to the atomic weights derived solely from the consideration of the equivalent quantities which enter into combination. Gmelin adopted the same ideas in the several editions of his great work, and contributed greatly in the course of time towards the introduction of the equivalent notation.

Berzelius made a concession upon one point to all these opponents. He introduced the idea of double atoms and applied it to certain gases, such as hydrogen, nitrogen, chlorine, bromine, and iodine, the atomic weights of which were only half those admitted by other chemists. These double atoms were supposed to enter into combination in pairs, and every pair represented precisely what others termed 'the proportion' or 'equivalent.' Water was therefore composed of a double atom of hydrogen united to one atom of oxygen, and this combination was represented by the symbol $\text{Ħ}O$. Hydrochloric acid and ammonia were formed, the first of one double atom of hydrogen united to one double atom of chlorine, the second of one double of nitrogen united to three double atoms of hydrogen. The formulæ $\text{Ħ}O$, ĦꞒl, $\text{Ħ}_3\text{N̶}$, were really equivalent to the formulæ H_2O, H_2Cl_2, H_6N_2, but remind us of the notation HO, HCl, H_3N, employed by Gmelin and others. It was, in fact, a step backwards. In admitting double atoms Berzelius unnecessarily doubled a number of formulæ; and if it is true that H_2O, H_2Cl_2, represent, from a certain point of view, equivalent quantities of water and hydrochloric acid, it is equally true that these formulæ do not represent true molecular magnitudes. Gerhardt subsequently showed that if a molecule of water, occupying two volumes of vapour, is represented by the formula HO, a molecule of hydrochloric acid occupying two volumes of vapour should be represented by the formula HCl, and a molecule of ammonia by H_3N. It is true that the formula H_2Cl_2 corresponds to the formula $PbCl_2$, $ZnCl_2$, $CaCl_2$, and KCl_2, by which Berzelius represented the chlorides of lead, zinc, calcium, and potassium. But we now know that the molecules of all these chlorides are not, strictly speaking, equivalent, and that if the three first are true the fourth must be halved. The law of specific heats forces us, in fact, to halve the atomic weight of potassium, and consequently to represent its chloride by the formula KCl, which answers to HCl. The latter formula represents two volumes of vapour, as do the formulæ of water, H_2O, and of ammonia, H_3N.

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[1] Among others the atomic weights of uranium, silicon, &c.

All these inaccuracies which we have pointed out in Berzelius's system of atomic weights and notations arose from an erroneous conception of the law of volumes. Instead of regarding as equidistant, and equally distributed in equal volumes of gases or vapours, the particles of the second order, or the molecules of simple and compound bodies, as Avogadro and Ampère had done, and later Gerhardt, Berzelius only considered the primordial atoms of certain simple gases, holding that they alone, and not the 'compound atoms,' are distributed in equal numbers in equal volumes. We know now that this is an erroneous idea, and that the hypothesis of Avogadro and Ampère, long forgotten, but restored to its due place of honour by Gerhardt, applies to the single molecules or particles of the second order, which, whether simple or compound, constitute the ponderable matter of gases and vapours.

CHAPTER IV.

SYSTEM OF CHEMICAL EQUIVALENTS—EQUIVALENT NOTATION

I.

THE interpretation which Berzelius had given of the law of volumes formed, as we have seen in the preceding pages, one of the foundations of his system of atomic weights and of his notation. This foundation was destroyed by the researches of Dumas, and subsequently of Mitscherlich, upon vapour densities commenced in 1827. Dumas noticed that the vapour density of mercury is sensibly equal to 100, hydrogen being taken as unity. The vapour densities of mercury and of oxygen are as 100 : 16 or as 50 : 8. If the atomic weights were proportional to the densities, 8 of oxygen should combine with 50 of mercury to form mercuric oxide. This is not the case; mercuric oxide is composed of 8 of oxygen and 100 of mercury, and it is the latter number which Berzelius had adopted for the atomic weight of mercury. If equal volumes of oxygen and of mercury vapour contain the same number of atoms, their densities should be in the ratio of 8 to 100, or, in other words, the density of mercury vapour is only half what it should be. We have here evidently a well-marked exception, or, better, a manifest contradiction between the facts and the principle admitted by Berzelius. Other exceptions may be mentioned. The vapour densities of sulphur and phosphorus determined by Dumas in 1832 were found to be, in the first case, three times as great, and in the second twice as great, as those indicated by theory. Chemical considerations have caused a composition, expressed by the formulæ H_2S and SO_3, to be attributed to sulphuretted hydrogen and sulphuric anhydride. From these formulæ the ratio between the atomic weights of sulphur, oxygen, and hydrogen is expressed by the numbers 32 : 1 : 16, and the densities should be in the same ratio. Now, the vapour density of sulphur taken at about 560° is 96, hydrogen being taken as unity. From this density a quantity weighing 32 in the molecule of sulphuretted hydrogen would not represent an atom of sulphur, but $\frac{1}{3}$ of an atom, and the formula of sulphuretted hydrogen, expressed in conformity with the law of volumes, would be $H_2S_{\frac{1}{3}}$, which is inadmissible.

From the formulæ PH_3 and P_2O_5, adopted for phosphoretted hydrogen and phosphoric anhydride respectively, the relation between the atomic weights of phosphorus, hydrogen, and oxygen should be expressed by the numbers 31 : 1 : 16. Now, the vapour density of phosphorus is equal to $2 \times 31 = 62$. If, therefore, the density of sulphur vapour is three times greater than that indicated by theory, that of phosphorus is twice as great. The case is the same with that of arsenic, from an experiment of Mitscherlich, who also confirmed, in 1833, the results obtained by Dumas upon the vapour of mercury, sulphur, and phosphorus.

We here, therefore, meet with a serious difficulty. For its solution two courses are open to us: we must either maintain the principle of the equality of the number of atoms in equal volumes of gases or vapours, and determine to assign to mercury, sulphur, phosphorus, and arsenic atomic weights which shall conform to the vapour densities, although they are less probable, and consequently to give their compounds the formulæ Hg_2O, $H_2S\frac{1}{3}$, $P\frac{1}{2}H_3$; or else it will become necessary to sacrifice the principle under discussion, in order to enable us to adopt the atomic weights, HgO, indicated by chemical analogies and the law of specific heats. The atomic weights of mercury, sulphur, phosphorus, and arsenic being, therefore, 200, 32, 31, 75, referred to hydrogen as unity, the preceding formulæ become HgO, H_2S, PH_3, and AsH_3.

It is the latter course which chemists have adopted, since they were properly unwilling to neglect more evident analogies. But the adoption of these atomic weights involves the following consequences:—

1. The vapour of mercury, the density of which is only half that required by the atomic weight assigned to mercury, evidently contains half the number of atoms contained in an equal volume of hydrogen.

2. The vapour of sulphur, which at 500° is three times as dense as it should be from the atomic weight assigned to sulphur, contains, at this temperature, three times the number of atoms contained in an equal volume of hydrogen.

3. The vapours of phosphorus and arsenic, which are twice as dense as they should be from their atomic weights, evidently contain twice as many atoms as an equal volume of hydrogen.

The atomic constitution of gases or of elementary vapours is not, therefore, always the same, as Berzelius for a long time supposed. If we compare elementary gases or vapours, as far as concerns the number of atoms which they contain, to the vapour of mercury, which contains the least, we shall have the result that, if mercury vapour contains in a certain volume one atom, hydrogen, oxygen, nitrogen, chlorine, bromine, and iodine contain 2, phosphorus and arsenic contain 4, while sulphur at 500° contains 6. The relations between the number of atoms contained in equal volumes of gases or of vapours may be obtained by dividing the density of the gas or vapour by the corresponding atomic weight. We shall thus obtain the following results :—

	Densities referred to Hydrogen	Atomic Weights	Densities divided by Atomic Weights. Number of Atoms in Unit of Volume	Number of Atoms in 2 Volumes
Mercury . .	100	200	0·5	1
Hydrogen . .	1	1	1	2
Oxygen . .	16	16	1	2
Nitrogen . .	14	14	1	2
Chlorine . .	35·5	35·5	1	2
Bromine . .	80	80	1	2
Iodine . . .	127	127	1	2
Phosphorus . .	62	31	2	4
Arsenic . .	150	75	2	4
Sulphur at 500° .	96	32	3	6

We have, therefore, to distinguish monatomic, diatomic, tetratomic, and hexatomic gases. Gmelin has already introduced into science a similar distinction, which has now become so important. At p. 54 of the first volume of the fourth edition of his treatise he gives a table analogous to the preceding, with some differences due to the different atomic weights adopted. Those used in our table are those of Berzelius (p. 62), which are now adopted for the respective elements.

With Gmelin and other chemists who soon followed his example it was different. As we have already remarked, the former maintained the proportional numbers which he designated in the first editions of his classical treatise by the erroneous term of 'Mischungsgewichte,'[1] and which he referred to hydrogen as unity, following the example of Dalton. In the fourth edition of his work he returns to the term atomic weights, but the numbers thus designated were identical with the proportional numbers or equivalents.

II.

The system of chemical equivalents and the notation derived from them gradually prevailed over the system of atomic weights and the notation of Berzelius, and are still preferred by some French chemists. It will therefore be useful to explain the principles upon which this equivalent notation rests, and particularly the arguments used by Gmelin against Berzelius in the question which forms the chief point of the discussion—

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[1] Literally 'mixing weights,' instead of 'combining weights.'

viz. the atomic weights of hydrogen, nitrogen, phosphorus, arsenic, chlorine, bromine, and iodine, which are half the proportional numbers or equivalents.

1. The atomic weights are deduced from the densities of the gases, and are founded upon the hypothesis that these gases contain an equal number of atoms in equal volumes. Now, this hypothesis is contradicted by experiment, as far as concerns the vapours of sulphur, phosphorus, arsenic, and mercury. Gmelin also remarked that certain gases — hydrochloric acid, for example—contain in equal volumes only half as many atoms as chlorine and hydrogen.[1]

There is, therefore, no reason for the adoption of the halved atomic weights of Berzelius, and his *double atoms* are the true atoms—that is to say, the equivalents.

2. The small atoms of which he speaks never enter singly into any combination. Neither do they ever enter into combination in uneven numbers, such as 3, 5, 7, &c., but always in even numbers, such as 2, 4, 6. Thus water contains H_2O, and hydrochloric acid H_2Cl_2, and ammonia H_6N_2. The atomic weights of hydrogen, chlorine, and nitrogen ought, therefore, to be doubled, so as to give the above compounds the simple formulæ HO, HCl, and H_3N.

3. We should admit that heterogeneous atoms unite in the simplest proportions, and the value of the atomic weights ought to be doubled in order to represent these simple relations. Thus, when a metal only combines with oxygen in a single proportion, it should

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[1] HCl was then called an atom of hydrochloric acid.

be supposed that the combination takes place *atom with atom*, unless isomorphism points to the contrary; and when a metal forms several combinations with oxygen, the strongest base ought to be supposed to be a combination of one atom of metal with one atom of oxygen.

4. The sum of all the atomic weights of an acid should represent the weight of the acid which saturates a quantity of base containing one atom of oxygen. Thus 40 parts of sulphuric acid saturate 111·8 parts of oxide of lead, which contain 8 of oxygen (one equivalent) and 103·8 of lead (one equivalent). These 40 parts consequently represent the sum of the equivalents of oxygen ($24 = 3 \times 8$) and of sulphur (16); 16 is therefore the equivalent of sulphur, the formula of sulphuric acid being SO_3. The question of equivalence is here very clearly put, almost in the terms used by Dumas in 1828 in the first volume of his celebrated treatise on chemistry applied to the arts.

5. The same formulæ ought to be assigned to isomorphous compounds as well as to compounds of the same order formed by simple and similar bodies, such as cobalt and nickel.

We will briefly examine into the value of these arguments,[1] reserving the development of some of the points here mentioned for the following chapter.

1. Gmelin justly observed that there are exceptions to the principle laid down by Berzelius of the equality of the number of atoms in equal volumes of a gas or a

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[1] No objection can be made to the last principle (No. 5), which is followed by all notations.

vapour, and that consequently the weights of equal volumes do not always represent the atomic weights This is admitted. But when he remarks that one volume of hydrochloric acid gas only contains half the number of atoms contained in one volume of chlorine or of hydrogen, he evidently confuses atoms with molecules. It is now admitted that equal volumes of these gases contain the same number of molecules, and we may remark that, in the present case, they also contain the same number of atoms, as is shown by the following formulæ :—

$H_2 = 2$ vol.	$Cl_2 = 2$ vol.	$HCl = 2$ vol.
1 molecule of hydrogen.	1 molecule of chlorine.	1 molecule of hydrochloric acid.

2. It is not correct to say that the small atoms of Berzelius do not enter into combination in uneven numbers. If a molecule of water is represented by the formula $H_2O = 2$ vol., a molecule of hydrochloric acid is represented by the formula $HCl = 2$ vol., and a molecule of ammonia by the formula NH_3. The double formulæ of Berzelius, H_2Cl_2 and N_2H_6, did not represent the true molecular masses; they were double the true number and ought to be halved, as was first proposed by Gerhardt. The small atoms of Berzelius, $H = 6{\cdot}24$, $Cl = 221{\cdot}3$, $N = 88{\cdot}5$, therefore represent the true atomic weights of these elements, referred to oxygen as 100, and the ratio between these numbers is identical with the ratio between the numbers 1 : 35·5 : 16, which are now accepted as the atomic weights of these elements.

3. The statement is correct that heterogeneous atoms generally unite together in very simple propor-

tions. This fact becomes evident if we allow ourselves to be guided in determining atomic weights and in constructing formulæ, not only by chemical considerations, but also by the great physical laws which have been described—namely, the law of volumes, of specific heats, and of isomorphism. Purely chemical considerations might lead us into error. Thus it is not correct to say that the strong bases ought always to contain *one* atom of metal and *one* atom of oxygen. Lime, baryta, strontia, cupric oxide, mercuric oxide, &c., contain, it is true, 1 atom of metal and 1 atom of oxygen; but oxide of silver, which is a strong base, contains 2 atoms of metal for 1 of oxygen, the atomic weight of silver being determined by the law of specific heats. As far as concerns oxide of silver, therefore, we make a mistake if we invoke analogy in order to connect it with the preceding oxides in respect to its atomic constitution.

4. The principle of equivalence made use of by Dalton, Wollaston, Gay-Lussac, and Gmelin for the determination of equivalents (which Dalton and Gmelin called atomic weights) would be admirable if it could be applied rigorously either to elements or to compounds.

But we now know that all atoms are not equivalent, and that the case is the same with molecules and with the reactions to which they give rise.

Atoms differ in their combining or substituting value—in their *valency*, as it is called—molecules in their state of condensation and their degree of saturation, and reactions in the greater or less extent of their complexity. As we have remarked above concerning oxides, it is impossible to cast all this in the same mould.

To return to the exact point of the discussion, it is impossible to consider a molecule of nitric acid and of phosphoric acid as equivalent; and if, in conformity with the rule laid down by Gmelin, 14 is the equivalent of nitrogen because nitrate of silver contains 14 parts of nitrogen for 108 of silver, 10·5 should be the equivalent of phosphorus, for it is the weight of phosphorus contained in a quantity of phosphate of silver containing 108 parts of silver. Now, all chemists admit that the equivalent of phosphorus is 31·4; but then we must no longer consider a molecule of nitric acid as equivalent to a molecule of phosphoric acid, for if the former saturates a quantity of oxide of silver containing 1 atom of silver, the latter saturates a quantity of oxide of silver containing 3 atoms. In fact, the discovery of polybasic acids proved a serious difficulty to the theory of equivalence; it showed that chemical molecules are not equivalent, as was shown for atoms by the law of volumes. Moreover, Gmelin felt that he had met with a difficulty, for he mentions polybasic acids as forming an exception to the theory of equivalence. It is sometimes said—I do not know for what reason—that exceptions prove the rule; in the present case they have become so numerous and so striking that they have overthrown it. The discovery of polybasic acids has, in fact, been supplemented by other discoveries, and they have completely modified the old ideas upon the equivalence of molecules and of reactions. But this is not the proper place to develope this point, and we will merely add a remark which seems important.

Dalton and Gay-Lussac alone applied true principles to the determination of equivalents. Dalton attributed to phosphorus the atomic weight 10·3; it represents the quantity of phosphorus which combines with 1 part of hydrogen: to carbon the atomic weight 4·3 (instead of 6); it represents the quantity of carbon which unites with 1 of hydrogen to form bicarburetted hydrogen. Gay-Lussac started from another point of view. Considering ordinary phosphate of soda as neutral, he admitted in this salt the presence of one equivalent of base and consequently one equivalent of sodium. He therefore expressed its composition by the formula $PO_{2\frac{1}{2}}.NaO + Aq$,[1] and attributed to phosphorus the proportional number 15·7. The quantity of neutral phosphate of soda which is proportional or equivalent to a molecule of nitrate of soda, $NO_5.NaO$, or of silver, $NO_5.AgO$, ought, in fact, only to contain 1 atom of metal, like the latter.

Applying the same principles in other cases, he wrote ferrous oxide FeO and ferric oxide $Fe\frac{2}{3}O$.

Ferrous sulphate, $SO_3.FeO$, was strictly equivalent to ferric sulphate, $SO_3.Fe\frac{2}{3}O$.

Berzelius, on the contrary, who had at last decided to admit the existence of sesquioxides, proved that they unite with 3 atoms (molecules) of acid. He consequently represented ferrous and ferric sulphates by the formulæ $SO_3.FeO$ and $3SO_3.Fe_2O_3$. Is it not evident that he was less consistent than Gay-Lussac, and that these formulæ do not represent equivalent quantities? It is only a strange abuse of language, not to say a logical error, to consider as equivalent a molecule of ferric oxide, which saturates 3 molecules of sulphuric acid, and a molecule of ferrous oxide, which only saturates 1 molecule. Formulæ analogous to those of the sulphates of the sesquioxides, such as those of the phosphates and of several other compounds, which are now distinguished by the name polyatomic, reveal, therefore, serious inconsistencies in the equivalent notation, and we must choose between such inconsistencies and the graver inconvenience of misrepresenting reactions by referring them to strictly equivalent proportions. This point will be developed in the following chapter.

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[1] $P = 15·7$; $O = 8$. At this time no account was taken of basic water. Gay-Lussac therefore involuntarily committed an error in the determination of the equivalent of phosphoric acid. In fact, the quantities of phosphate of soda and of nitrate of silver which enter into reaction, and which are strictly equivalent, are $\frac{1}{3}(PO_4Na_2H)$ and NO_3Ag, and the quantity of phosphorus in $\frac{1}{2}(PO_4Na_2H)$ is 10·5. This is the number of Dalton.

The preceding discussion renders it sufficiently evident that the system of chemical equivalents, and of the notation derived from them, introduced by Dalton, Wollaston, Davy, Gay-Lussac, and Gmelin, were based upon too narrow a foundation for the enlarged edifice of chemistry. Our present system of atomic weights and our notation rest upon a wider foundation. Their establishment has required the numerous efforts which have been perseveringly maintained for a period of thirty years.

CHAPTER V.

PRESENT SYSTEM OF ATOMIC WEIGHTS.

GERHARDT AND LAURENT—CANNIZZARO.

I.

THE equivalent notation of the English chemists and of Gay-Lussac, which was adopted by Liebig and defended by Gmelin in 1843, had, at the period of which we are speaking, gained the almost unanimous approval of chemists; they were struck with the exceptions presented by the law of volumes as it was then interpreted, by the useless complication which the conception of the double atoms of Berzelius had introduced into a large number of formulæ, and they were satisfied with the more simple expressions which the notion of equivalents offered for chemical reactions and combinations. The law of volumes was entirely sacrificed. The equivalents of hydrogen, nitrogen, chlorine, &c., corresponded to two volumes, whilst that of oxygen only constituted one. The formulæ of water, HO, of sulphuretted hydrogen, HS, of protoxide of nitrogen, NO, expressed two volumes; those of hydrochloric acid, HCl, of ammonia, NH_3, of phosphoretted hydrogen, PH_3, &c., represented four.

Gerhardt was the first to draw attention to these errors, and to the necessity of considering as equivalents quantities of water, ammonia, hydrochloric acid, &c., corresponding to equal volumes. Regarding water, H_2O, as formed of two atoms or volumes of hydrogen and as occupying 2 volumes, if one atom of hydrogen occupies one volume. he compares it to hydrochloric acid, HCl, formed of one atom or volume of hydrogen and of one atom or volume of chlorine, and occupying 2 volumes; to ammonia, NH_3, formed of one atom (volume) of nitrogen and of 3 atoms (volumes) of hydrogen, and occupying 2 volumes. In the same manner the formulæ N_2O, NO, CO, CO_2, CH_4, C_2H_4, which correspond to 2 volumes, represent molecules (Gerhardt still used the term equivalents) of protoxide of nitrogen, dioxide of nitrogen, carbonic oxide, carbonic acid, and of marsh gas and olefiant gas. The atomic weights on which the preceding formulæ are founded are the same as those of Berzelius, i.e. $O=100$, $H=6{\cdot}25$, $N=88$, $C=75$. But the formulæ of hydrochloric acid, H_2Cl_2, of ammonia, N_2H_6, of marsh gas, C_2H_8, of olefiant gas, C_4H_8, which Berzelius had employed were halved and made to represent 2 volumes. Here lies the true progress.

It will be interesting to recall the considerations which led Gerhardt to propose this reform in the notation of Berzelius.

Regarding a molecule of water as formed of 2 atoms of hydrogen and 1 atom of oxygen, and carbonic acid as containing 1 atom of carbon and 2 atoms of oxygen, he was struck, in the attentive study of the reactions of organic chemistry, by the fact that in none of these reactions, represented by the formulæ and equations of Berzelius then in use, were quantities of water and carbonic acid corresponding to H_2O and CO_2 set free, but that the quantities formed were never less than those corresponding to the formulæ H_4O_2 and C_2O_4.

We may therefore conclude, he says, that an error has been committed in the construction of organic formulæ, for it would be strange if no reaction should give rise to the formation of a single molecule of water or a single molecule of carbonic acid. This is the error: organic formulæ are twice as great as they should be, and must be halved, as well as the atomic weights of metals. These two facts are correlative, and it was precisely those high atomic weights attributed by Berzelius to the metals which gave to organic compounds formulæ double what they should be. Thus amongst the organic combinations with which we are most fully acquainted we must reckon the acids; their molecular magnitude is determined by their capacity of saturation, and we admit that a molecule of acid saturates a molecule of basic oxide—that is to say, a quantity of base containing one atom of metal. Thus, for example, the formula of acetic acid is constructed by combining it with oxide of silver and analysing the acetate of silver. The composition of this salt, containing one atom of silver, is represented by the formula $C_4H_6AgO_4$, derived from the atomic weights $C=75$, $H=6{\cdot}25$, $O=100$, $Ag=1351{\cdot}6$, which are those of Berzelius. But upon halving the atomic weight of silver we obtain Ag = 675·8; the preceding formula will become $C_4H_6Ag_2O_4$; and there is no reason why we should not halve this, for we must admit that the monobasic acetic acid only contains in its salts a single atom of metal. The true formulæ of acetate of silver and acetic acid are therefore $C_2H_3AgO_2$ and $C_2H_4O_2$.

But why must we halve the atomic weights of metals in this manner? In order that their oxides may be comparable to water. If the latter is formed of 2 atoms of hydrogen, we may reasonably attribute to protoxides a similar composition, and represent them by the formula M_2O instead of MO. Oxide of potassium and oxide of silver being, therefore, K_2O and Ag_2O, the atomic weights of potassium and silver will be 245 and 687·5 [1]—that is to say, the half of those attributed to them by Berzelius, the atomic weights of hydrogen and oxygen being 6·25 and 100. Applying the same considerations to the other protoxides, Gerhardt also halved the atomic weights of the metals which they contain. We shall presently see that in this he went too far; but this reasoning was perfectly correct as far as it concerned acetate of silver, and nothing could be more legitimate than the halving of the formula of acetic acid, the unnecessary complication of which he was the first to show. And this change demanded others. It is clear that the several monobasic acids, the alcohols, ethers, amides, &c., must be represented by formulæ which harmonise with that of acetic acid.

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[1] The number 687·5 is deduced from a determination of Erdmann and Marchand (*Précis de Chimie organique*, t. i. p. 54).

This led to an important reform in the notation of organic compounds, which reform extended even to inorganic compounds. Berzelius had represented hydrochloric acid by the formula H_2Cl_2, because 100 being the atomic weight of oxygen, this quantity of hydrochloric acid was necessary to saturate a molecule of oxide of silver containing 1351·6 of silver and 100 of oxygen. The formula H_2Cl_2 is therefore in harmony with the formulæ KCl_2, $AgCl_2$, $PbCl_2$, which represent the composition of the protochlorides. But when the atomic weights of the metals were halved, it was considered advisable to attribute to all these chlorides the more simple formulæ HCl, KCl, AgCl, PbCl.

The reform which Gerhardt introduced into notation necessitated certain modifications in the existing ideas concerning the constitution of salts. It can now no longer be said that a molecule of acetate of silver contains a molecule of anhydrous acetic acid and a molecule of oxide of silver, or that hydrated acetic acid contains a molecule of anhydrous acid and a molecule of water. The double formulæ favoured these interpretations, while the simple formulæ cannot be divided in such a manner. Though $C_4H_6Ag_2O_4$ might be decomposed into $C_4H_6O_3+Ag_2O$, and $C_4H_8O_4$ into $C_4H_6O_3+H_2O$, the formulæ $C_2H_3AgO_2$ and $C_2H_4O_2$ could not be divided so as to give anhydrous acid and oxide of silver, or anhydrous acid and water. Yet the relations between acetic acid and acetate of silver are very simple, and correctly defined when we say that acetate of silver consists of acetic acid in which one atom of hydrogen is replaced by an atom of silver. The molecule of acetic acid may, then, be regarded as a group of atoms in which an atom of hydrogen, which is called basic, can be replaced by an atom of metal, in the same manner as, in a different class of facts, the three other atoms of hydrogen may be replaced by three atoms of chlorine.

This is an important consequence of Gerhardt's notation, to which I thought it well to draw attention in passing, for these ideas upon the nature of salts were opposed by their great author to the dualistic theory, and are in harmony with the proposition which was at that time supported by Dumas, Laurent, and the advocates of the substitution theory, which teaches that chemical combinations form a whole, a unit. This was at that time—perhaps improperly—called the unitary system.

But to return to the point under discussion: I have just mentioned Laurent, and we should notice the fact that he was the first adherent of Gerhardt's system of atomic weights and notation. I think it will be also interesting to recall some of the ideas which he then published in connection with this notation.

We admit that oxide of potassium is formed of 2 atoms of potassium and 1 atom of oxygen, but caustic potash or potassium hydrate cannot be regarded as containing the elements of oxide of potassium + the elements of water. The molecule of potassium hydrate may be compared on the one hand to that of oxide of potassium, on the other to that of water, and is derived in a manner from the latter by the substitution of an atom of potassium for an atom of hydrogen.

Thus water, potash, and anhydrous oxide of potassium are compounds of the same order containing respectively a single atom of oxygen combined either with 2 atoms of hydrogen, 2 atoms of potassium, or with 1 atom of potassium and 1 atom of hydrogen. The metallic hydrates are, therefore, compounds of the same order as the oxide, and cannot be represented as containing an anhydrous oxide + water. But there are also organic hydrates and oxides; and if we admit, in alcohol and ether, the existence of an ethyl group, so termed by Berzelius, we shall observe the same relations between water, alcohol, and ether as those which exist between water, potash, and oxide of potassium. Alcohol becomes ethyl hydrate, and ether ethyl oxide. The following formulæ, in which Et represents the ethyl group C_2H_5, will show these analogies:—

H_2O, water.	H_2O, water.
KHO, potassium hydrate.	EtHO, alcohol.
K_2O, potassium oxide.	Et_2O, ether.

This grand generalisation was afterwards extended by Gerhardt, who had first discovered the acid chlorides and anhydrous monobasic acids, to the acids. Upon comparing AcCl, chloride of acetyl, with EtCl, chloride of ethyl, and hydrochloric acid, the same kind of relations were discovered between acetic acid and anhydrous acetic acid as those between alcohol and ether. The salts and ethers of acetic acid can, as Williamson has shown, be added to this synoptic table, which formed the basis of the celebrated idea of considering hydrochloric acid and water as types:—

HCl, hydrochloric acid.
$EtCl$, chloride of ethyl.
$AcCl$, chloride of acetyl.
KCl, chloride of potassium.

H_2O, water.
$AcHO$, acetic acid.
$AcKO$, acetate of potassium.
$AcEtO$, acetic ether.
Ac_2O, acetic anhydride.

It is from the new notation that these views, which embrace the discoveries of Williamson on etherification and those of Gerhardt on anhydrous acids, derive their simple and striking forms. The molecules of all the bodies just mentioned are comparable, under the condition that they are represented, in accordance with the principles developed by Gerhardt, by formulæ which represent the true molecular magnitudes. And it is important to remark that all these formulæ correspond, in the case of volatile compounds, to 2 volumes of vapour. 'We halve,' he says, 'organic and mineral formulæ, so as to express their *equivalent* by 2 volumes.' 'Equivalent' is used instead of 'molecule,' and from the preceding proposition we conclude that equal numbers of the molecules of gaseous or volatile compounds are contained in equal volumes of gases or vapours. This is the law of Avogadro and Ampère, which reappears as a guiding star upon the horizon after a long eclipse. And yet we cannot say that Gerhardt, at this period at at least, gave himself up entirely to its guidance. The considerations by which he was principally influenced were rather of a purely chemical character—those which we have alluded to above. They were correct, and were found to agree with an equally correct idea which had been forgotten. The distinction between two species of minute particles, molecules and atoms, which Avogadro and Ampère had introduced without effect into science, and which Dumas had endeavoured to reproduce in his 'Chemical Philosophy,' was probably mentally clear to Gerhardt, though as yet it had not appeared in his writings. The word 'equivalent' was sometimes synonymous with the term 'molecule,' sometimes with 'atom' or 'volume.' To quote his own words, 'Therefore,' he says in p. 51 of his 'Précis,' '*volumes, atoms, and equivalents* are synonymous in the case of simple bodies. It therefore follows that the *densities of simple gases are proportional to their equivalents*.' These propositions were not new, but they were inaccurate. These inaccuracies soon disappeared, and the distinction between molecules and atoms appeared clearly in the classic 'Traité de Chimie organique.'

Gerhardt's system of atomic weights, which was immediately adopted by Laurent, gradually gained the approval of a great number of chemists. His works upon the theory of types, the discovery of the anhydrides and the chlorides of the monobasic fatty acids, gave him great authority, which profited him but little personally, but which will always be connected with his name. The simplicity of the new notation gave great clearness to the explanation of new facts and ideas. In England Williamson, Odling, Brodie, Frankland, Hofmann, Gladstone, Roscoe, and others successively adopted this notation. The new German school, which was then under the brilliant direction of Kekulé and Baeyer, adopted it at once, as also has been the case with the greater number of Russian and Italian chemists. In France Chancel has always made use of it, and I myself did so in my memoir upon the glycols in 1858.

II.

The commencement of the year which I have just mentioned was, however, marked by the introduction of an important change. Cannizzaro proposed once more to double the atomic weights of a great number of metals. We must now point out the facts and follow the course of ideas which have proved the reform introduced by the illustrious Italian to be legitimate and gained for it the almost unanimous approbation of chemists.

Gerhardt's atomic weights were not true equivalents, and molecules which occupy the same volume in a gaseous state are not always compounds of the same degree or the same order; for Gerhardt afterwards referred these compounds to three different types—the hydrogen or hydrochloric acid type, the water type, and the ammonia type. That the molecules of chemical compounds differ from each other in their type—that is to say, in their degree of complication or in their manner of condensation (which, moreover, the discoveries of Gay-Lussac had already indicated)—and consequently that molecules belonging to different types are not strictly equivalent, was an idea which was gaining ground in science. Correctly speaking, it was not at that time perfectly new; since the admission of the existence of sesquioxides, such as alumina and ferric oxide, it had been found that their capacity of saturation was three times greater than that of the protoxides; the sesquioxides are polyacid bases.

On the other hand, Graham had already made the great discovery of polybasic acids.

But other facts were soon added to the preceding, which introduced into science, if not the fact, at least the clearly defined notion of polyatomic compounds. I allude especially to the works of Berthelot upon glycerine, which produced such a number of important results, to which, I believe, I was the first to give their true interpretation in the order of ideas which we are now discussing. I must also mention Berthelot's work upon the sugars and my own researches upon radicals and glycols, in which I endeavoured to define the part played by radicals in polyatomic compounds. These researches have introduced into science the idea that all chemical molecules are not mutually equivalent as far as their molecular complication is concerned, or, to use the phraseology of that time, 'the degree of condensation affected in them by matter.'[1] In order to define the differences which they present in this relation, they were referred to more or less condensed types. Thus, to take a few examples, the constitution of nitric, sulphuric, phosphoric, acetic, and oxalic acids were represented by the following formulæ:—

$$\begin{array}{ccc}
\text{Type } \left.\begin{matrix}H\\H\end{matrix}\right\}O & \text{Type } \left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2 & \text{Type } \left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_3 \\
\hline
\left.\begin{matrix}(NO_2)'\\H\end{matrix}\right\}O & \left.\begin{matrix}(SO_2)''\\H_2\end{matrix}\right\}O_2 & \left.\begin{matrix}(PO)'''\\H_3\end{matrix}\right\}O_3 \\
\text{Nitric acid.} & \text{Sulphuric acid.} & \text{Phosphoric acid.} \\
\left.\begin{matrix}(C_2H_3O)'\\H\end{matrix}\right\}O & \left.\begin{matrix}(C_2O_2)''\\H_2\end{matrix}\right\}O_2 & \\
\text{Acetic acid.} & \text{Oxalic acid.} &
\end{array}$$

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[1] *Annales de Chimie et de Physique*, 3e série, t. xliv. p. 308.

Similar formulæ represented the constitution and the increasing complication of the molecules of potash and ferric hydrate, for example, and of those of alcohol, glycol, and glycerine:—

TYPE $\left.\begin{matrix}H\\H\end{matrix}\right\}O$	TYPE $\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2$	TYPE $\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_3$
$\left.\begin{matrix}K'\\H\end{matrix}\right\}O$ Potash.	"	$\left.\begin{matrix}Fe'''\\H_3\end{matrix}\right\}O_3$ Ferric hydrate.
$\left.\begin{matrix}(C_2H_5)'\\H\end{matrix}\right\}O$ Alcohol.	$\left.\begin{matrix}(C_2H_4)''\\H_2\end{matrix}\right\}O_2$ Glycol.	$\left.\begin{matrix}(C_3H_5)'''\\H_3\end{matrix}\right\}O_3$ Glycerine.

These typical formulæ had an advantage. They clearly indicated the fact that not only inorganic or organic radicals, but even simple bodies are capable of replacing 1, 2, or 3 atoms of hydrogen, and consequently differ in their substituting value. A distinction was therefore drawn between the monatomic, diatomic, and triatomic radicals. And as these radicals are in a manner nothing more than the representatives of the elements themselves, the distinction was extended to the latter. We shall presently develope this idea, that the power of combination or substitution with which radicals are endowed is essentially connected with that of the elements which they contain. But for a moment we must be contented with remarking that there is a gap between potash, which contains monatomic potassium, and ferric hydrate, which contains triatomic iron.[1] This gap has been, thanks to Cannizzaro, in a great measure filled up. This eminent chemist has doubled the atomic weights of a great number of metals, to bring them into harmony with the law of Dulong and Petit and the law of Avogadro. These metals have been regarded, therefore, as diatomic. Their oxides have become RO. Their hydrates, $\left.\begin{matrix} R'' \\ H_2 \end{matrix}\right\} O_2$, answered to the hydrates of the diatomic radicals—for example, to ethylene hydrate or glycol—which is given in the preceding table. We must not forget the influence which the discoveries of organic chemistry, and the interpretation given to them, have exercised upon the general conceptions of chemistry, and even upon the progress of mineral chemistry. We shall, therefore, return to this point in treating of atomicity.

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[1] The formula $\left.\begin{matrix}Fe'''\\H_3\end{matrix}\right\}O_3$, which has been proposed by Odling, clearly expresses this idea of triatomic iron. Fe''' here takes the place of H_3 in three molecules of water, $\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_3$

We here give the list of atomic weights now adopted by the majority of chemists. And, in order that the changes which the new discoveries and the progress of the theory have successively introduced into the system of atomic weights may be appreciated, we have, in the following table, marked elements with a distinctive sign. Those which are printed in *italics* represent the elements to which Berzelius and Gerhardt attributed the same atomic weights, which they now retain; those which are marked by an asterisk have retained Gerhardt's atomic weights; those, finally, which are marked by two asterisks are the metals whose atomic weights were halved by Gerhardt and doubled again by Cannizzaro, these double numbers being, moreover, those of Berzelius (see p. 62):—

	Symbols.	Atomic Weights.
Hydrogen	H	1
Aluminium*	Al	27·5
Antimony*	Sb	122
Arsenic	As	74·9 (75)
Barium**	Ba	137·2
Bismuth**	Bi	210
Boron*	B	11
Bromine	Br	80
Cadmium**	Cd	111·6
Cæsium	Cs	132·15
Calcium**	Ca	39·9
Carbon	C	12
Cerium	Ce	141·3
Chlorine	Cl	35·5
Chromium	Cr	52·4
Cobalt**	Co	58·6
Copper**	Cu	63·3
Didymium	Di	147 (?)
Erbium	Er	170·6
Fluorine	F	19·1
Gallium	Ga	69·9
Glucinum	G	9·25
Gold**	Au	196·2
Indium	In	113·4
Iodine	I	127
Iridium**	Ir	196·7
Iron**	Fe	55·9
Lanthanum	La	92
Lead**	Pb	206·4
Lithium*	Li	7·022
Magnesium**	Mg	24
Manganese**	Mn	54·8
Mercury**	Hg	200
Molybdenum**	Mo	95·8
Nickel**	Ni	58·6
Niobium	Nb	94
Nitrogen	N	14·044
Osmium**	Os	198·6
Oxygen	O	15·96 (16)

	Symbols.	Atomic Weights.
Palladium**	Pd	106·2
Phosphorus	P	31
Platinum	Pt	196·7
Potassium*	K	39·137
Rhodium**	Rh	104·2
Rubidium*	Rb	85·2
Ruthenium	Ru	103·5
Selenium	Se	78
Silicon*	Si	28
Silver*	Ag	108[1]
Sodium*	Na	23·043
Strontium**	Sr	87·2
Sulphur	S	31·98 (32)
Tantalum	Ta	182
Tellurium	Te	128
Thallium	Tl	203·6
Thorium	Th	233·9
Tin**	Sn	117·8
Titanium**	Ti	48
Tungsten**	W	184
Uranium	U	120
Vanadium	V	51·2
Yttrium	Y	89·6
Zinc**	Zn	64·9
Zirconium	Zr	90

The limits which are imposed upon us by the character of this work make it impossible to mention the methods which have been employed in each particular case for the determination of the atomic weights given in the preceding table. We must refer our readers for these details to the article upon Atomic Weights in the 'Dictionnaire de Chimie pure et appliquée.'

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[1] We have retained 108 as the atomic weight of silver, founding our opinion upon a recent observation of Dumas. Stas gave the number 107·93. The atomic weights of chlorine, bromine, and iodine being dependent upon that of silver, we have also retained the round numbers 35·5, 80, 127, as their atomic weights.

We would especially draw the attention of the reader to the methods employed by Stas in the determination of the atomic weights of oxygen, sulphur, chlorine, bromine, iodine, nitrogen, potassium, sodium, lithium, and silver, giving results the accuracy of which is unsurpassed. We must also mention the labours and analyses of Marignac, and to the names of the two chemists we have just mentioned must be added the great name of Berzelius. However, setting aside the question of practical chemistry, to which we have just alluded, we must confine ourselves to the theoretical discussion which has justified the adoption of the new system of atomic weights.

We shall endeavour to show that the atomic weights given in the preceding table are in harmony—first, with the law of Avogadro and Ampère; secondly, with the law of Dulong and Petit; thirdly, with the law of isomorphism. We shall then devote a chapter to the proof of the fact that the chemical and physical properties of elements are dependent upon the atomic weights. We shall prove, lastly, that the notation which is derived from the present system of atomic weights ascribes to compounds their true molecular magnitudes, and allows a correct representation of chemical reactions.

III.

The new system of atomic weights is founded upon the law of volumes, and is in harmony with the hypothesis of Avogadro and Ampère.

The 'law,' as it is generally called, of Avogadro and

Ampère may be enunciated as follows: *Equal volumes of gases or vapours*[1] *contain the same number of molecules.* We have here two things, a group of facts and an hypothesis.

The facts are a result, or rather a development, of the laws of Gay-Lussac.

Gay-Lussac had shown—first, that gases combine in simple volumetric relations; secondly, that there is a simple relation between the volumes of the combining gases and that of the product of the combination. To these two laws may be added a third. There is a very simple relation between the volumes of all compound gases thus formed, and the *hypothesis* of Avogadro and Ampère consists in the assertion that all these compound gases occupy the same volume, and that the matter thus condensed into the same volume exactly represents the ultimate particles of the compounds—that is to say, the molecules.

The accompanying table will explain our meaning:—

2 vol. hydrogen + 1 vol. oxygen give 2 vol. water.
2 vol. chlorine + 1 vol. „ „ 2 vol. hypochlorous anhydride.
2 vol. nitrogen + 1 vol. „ „ 2 vol protoxide of nitrogen.
1 vol. „ + 1 vol. „ gives 2 vol. dioxide of nitrogen.
1 vol. chlorine + 1 vol. hydrogen „ 2 vol. hydrochloric acid gas.
1 vol. nitrogen + 3 vol. „ „ 2 vol. ammonia.
1 vol. carb. oxide + 1 vol. chlorine „ 1 vol. oxychloride of carbon.
1 vol. ethylene + 1 vol. „ „ 1 vol. ethylene chloride.

We here have clear examples of the two laws of Gay-Lussac (see p. 34), as well as of the third law of volumes. Between the volumes of the compound gases we have the very simple relation 2 : 1. The hypothesis of Avogadro consists in the assertion that this relation is still more simple, that it is 2 : 2, for the smallest quantity or the ultimate particle of oxychloride of carbon and of ethylene chloride which can be formed does not occupy 1 volume, but 2 volumes. This is an hypothesis, if you will, but one the truth of which is easily demonstrated, for experiment shows that the smallest quantity of carbonic oxide which enters into reaction occupies two volumes, which contain a single volume of oxygen; it shows, moreover, that the ultimate particle or the molecule of oxychloride of carbon corresponds to the ultimate particle or molecule of carbonic acid gas, which occupies two volumes.

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[1] Under the same conditions of temperature and pressure.

These considerations apply to ethylene chloride and to other compounds. Consequently it is better to express the formation of oxychloride of carbon and of ethylene chloride in the following manner:—

2 vol. carbonic oxide + 2 vol. chlorine = 2 vol. oxychloride of carbon.
2 vol. ethylene + 2 vol. chlorine = 2 vol. ethylene chloride.

The two volumes thus formed represent the molecules of gases or vapours, and we are therefore led to give the following form to the statement of the law of Avogadro and Ampère.

The molecules of compounds which are gaseous or volatile without decomposition occupy two volumes, if an atom of hydrogen occupies one volume. This proposition holds good in the case of by far the greater number of volatile compounds, under the condition that their true molecular weights are attributed to these compounds.

The proofs are so abundant that it is impossible to quote all the examples, and we must confine ourselves to giving a list of the groups of compounds which obey the law in question.

Water and its analogues, sulphuretted hydrogen, &c.	H_2O	= 2 vol.
Hydrochloric acid and its analogues	HCl	= 2 vol.
Ammonia and its mineral and organic analogues; substitution derivatives of ammonia; organo-metallic radicals of the type RX_3	NH_3	= 2 vol.
Oxides and anhydrides of chlorine, nitrogen, sulphur, and carbon	Cl_2O	= 2 vol.
	ClO_2	= 2 vol.
	N_2O	= 2 vol.
	NO	= 2 vol.
	NO_2	= 2 vol.
	SO_2	= 2 vol.
	SO_3	= 2 vol.
	CO	= 2 vol.
	CO_2	= 2 vol.
	COS	= 2 vol.
All hydrocarbons	CH_4	= 2 vol.
	C_2H_4	= 2 vol.
	C_2H_6	= 2 vol.
	C_2H_2	= 2 vol.
	C_6H_6	= 2 vol.
	$C_{10}H_8$	= 2 vol.
	$C_{10}H_{16}$	= 2 vol.
	$C_{14}H_{10}$	= 2 vol.
Chlorides, bromides, and iodides of the metalloids and metals	BCl_3	= 2 vol.
	$SiCl_4$	= 2 vol.
	PCl_3	= 2 vol.
	PCl_5	= 2 vol.
	$AsCl_3$	= 2 vol.
	$SbCl_3$	= 2 vol.
	$POCl_3$	= 2 vol.
	CCl_4	= 2 vol.
	$COCl_2$	= 2 vol.
	$HgCl_2$	= 2 vol.
	$SnCl_4$	= 2 vol.
	Al_2Cl_6	= 2 vol.
	Fe_2Cl_6	= 2 vol. &c. &c.

Mercuric sulphide		HgS	= 2 vol.
Alcohols, glycols, phenols		C_2H_6O	= 2 vol.
Their anhydrides, such as	ethyl oxide	$(C_2H_5)_2O$	= 2 vol.
	ethylene oxide	C_2H_4O	= 2 vol.
Aldehydes and acetones	aldehyde	C_2H_4O	= 2 vol.
	acetone	C_3H_6O	= 2 vol.
Organic acids, such as acetic acid		$C_2H_4O_2$	= 2 vol.
Their anhydrides	acetic anhydride	$C_4H_6O_3$	= 2 vol.
	succinic anhydride	$C_4H_4O_3$	= 2 vol.
Their ethers, such as	ethyl acetate	$C_2H_3O_2(C_2H_5)$	= 2 vol.
	ethylene acetate	$(C_2H_3O_2)_2C_2H_4$	= 2 vol.
	ethyl oxalate	$C_2O_4(C_2H_5)_2$	= 2 vol. &c. &c.

This table is undoubtedly very much abridged, but it is evident that it embraces a vast number of mineral and organic compounds, and it is difficult to imagine how, in the presence of such a wealth of facts and proofs, accumulated by the labours of the last fifty years, some chemists should still refuse or hesitate to believe the law of Avogadro and Ampère. It is useless for them to bring forward some cases which apparently form exceptions, and which we shall presently mention and discuss. In fact, we may say that the other physical and chemical laws of which we have spoken—the law of Dulong and Petit and that of isomorphism—do not rest upon such a number of imposing facts, and consequently upon such a solid foundation, as the law of Avogadro and Ampère.

When a theoretical idea is true, the exceptions which are at first admitted gradually disappear, either because the new observations are more accurate than the old, or from a more correct interpretation of the facts. It also sometimes happens that these exceptions give rise to interesting developments of the theory and to a more extended generalisation.

That it has been so in the case before us we will now proceed to show.

I. Thirty years ago ordinary ether was represented by the formula C_4H_5O, which answered to two volumes, while the formula of alcohol, $C_4H_5O.HO$, answered to four volumes of vapour. Here was an exception to the law of volumes. Williamson came forward and showed that the old formula of ether should be doubled. The doubled formula, $C_8H_{10}O_2$, which in the new notation becomes $C_4H_{10}O$, corresponds to that of alcohol, C_2H_6O, both representing two volumes of vapour. It is unnecessary to insist upon the proofs which Williamson has given in his masterly memoir, and which are well known to all chemists—namely, the existence of mixed ethers, and the perfect agreement between the physical properties of these ethers and those of ordinary ether, under the condition that the latter is regarded as a double molecule of the form $(C_2H_5)_2O$.

II. According to Gerhardt's notation, which is still applied to organic compounds, monatomic hydrates do not contain the elements of water, but merely the residue OH. Thus acetic acid is acetyl hydrate, $C_2H_3O.OH$, and it is obviously impossible to separate from this formula the elements of water, H_2O, which could be done with the old formula of Berzelius $C_4H_8O_4 = C_4H_6O_3\,H_2O$, or with the formula in equivalents $C_4H_4O_4 = C_4H_3O_3.HO$. Thus it was the opinion of Gerhardt that the anhydrides of monobasic acids could not exist, and he had the singular fortune to discover them himself. But at the same time he showed, in striking confirmation of his ideas and formulæ, that in order to lose water the molecules of acetic acid must act in pairs, one of the molecules furnishing an atom of hydrogen, the other the residue OH.[1] The anhydride formed, $(C_2H_3O)_2O$, or acetyl oxide, answers to two volumes of vapour.

III. An analogous case occurred with the hydrocarbons called alcohol radicals, methyl, ethyl, &c. These are imaginary forms, said Laurent and Gerhardt, and have no separate existence. Kolbe and Frankland isolated them, but showed that their formulæ must be doubled.[2] Free ethyl is not composed of two atoms of carbon and five of hydrogen, as the group C_2H_5 in ethyl hydrate or alcohol, $C_2H_5O.OH$, but of $C_4H_{10} = (C_2H_5)_2$, and this doubled formula corresponds to two volumes of vapour.

The result of this is that the molecular weights of volatile compounds are accurately given by their densities. And if we refer these densities to that of hydrogen taken as unity, we have only to multiply the numbers obtained by 2 to find the weight of the molecules compared with that of an atom of hydrogen $= 1$. This is a general rule. The density referred to hydrogen is the weight of one volume.

The molecular weights are the weights of two volumes, for molecules occupy two volumes if an

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[1] Subjoined is the equation which expresses this dehydration of acetic acid—

$$\begin{matrix}C_2H_3O.OH\\C_2H_3O.OH\end{matrix} = H_2O + \left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\} O$$

Two molecules of acetic acid. Acetic anhydride.

[2] 'Mémoire sur une nouvelle Classe de Radicaux organiques,' *Ann. de Chim. et de Physique*, 3^e sér., t. xliv. p. 275.

atom of hydrogen occupies one; we must, therefore, multiply densities by 2 in order to obtain molecular weights.

The atomic weights of a certain number of metalloids and metals may be calculated from the molecular weights. Thus the atomic weights of phosphorus, arsenic, antimony, carbon, silicon, titanium, tin, mercury, and lead may be calculated from the molecular weights of the corresponding chlorides and ethides. For example—

The molecular weight of chloride of silicon (obtained by doubling its vapour density) is 170, and analysis shows that 170 parts of chloride of silicon contain $142 = 4 \times 35{\cdot}5$ of chlorine and 28 of silicon. The vapour density and analysis of chloride of silicon assign, therefore, to this body the formula $SiCl_4$, and to silicon the atomic weight 28, for we have reasons for the belief that the molecule of chloride of silicon only contains a single atom of silicon.

The vapour density of zinc ethyl doubled = 123, the density of hydrogen being = 1. Now, analysis shows that these 123 parts of zinc ethyl contain two ethyl groups, which weigh 58, and 65 parts of zinc. 65 is the atomic weight of zinc, the composition of zinc ethyl being expressed by the formula $Zn(C_2H_5)_2$. The number 65 (64·9) is, moreover, confirmed by the law of specific heats.

The molecular weight of mercuric chloride, calculated from its vapour density, is 271, and analysis shows that these 271 parts of mercuric chloride contain $2 \times 35{\cdot}5 = 71$ of chlorine and 200 of mercury. Hence the simplest composition which can be assigned to mercuric chloride is represented by the formula $HgCl_2$, Hg being an atom of mercury. The atomic weight of mercury is thus fixed at 200, a number which agrees with the law of specific heats.

According to the invaluable experiments of H. Sainte-Claire Deville and Troost, the vapour density of ferric chloride assigns to this compound the molecular weight 325. Now, 325 parts of ferric chloride contain $213 = 6 \times 35{\cdot}5$ of chlorine and 112 (111·8) of iron. Are one or more atoms of iron represented by these 112 parts? In this case we should no longer prefer the simplest hypothesis, as in the preceding cases. The law of specific heats attributes to iron the atomic weight 56 (55·9); we must, therefore, admit that ferric chloride contains two atoms of iron, and six of chlorine, and that its composition is represented by the formula Fe_2Cl_6.

These examples show the use which may be made of the law of Avogadro and Ampère in the determination of molecular weights and in settling atomic weights.

We also see the assistance which chemists derive from the law of Dulong and Petit, when they have to choose between several molecular formulæ for a given compound, and consequently between several atomic weights for the same element.

The considerations mentioned above apply to a great number of cases. That this is so will be seen from the following table,[1] which shows the part played by the law of volumes, firstly in the determination of molecular weights, and subsequently in that of atomic weights. The experimental densities given in the third column are referred to that of air taken as unity. To refer them to the density of hydrogen we have only to multiply them by the number 14·44, which expresses the relation which the density of air bears to that of hydrogen. The figures in the fourth column express the double densities referred to hydrogen, and consequently the weight of two volumes, 1 standing for the weight of one volume of hydrogen. They were obtained by multiplying these densities by 28·88. They are the same as the molecular weights given in the fifth column. Lastly, the sixth column[1] gives the molecular composition: it shows the weights of the elements contained in the molecule, and consequently the atomic weights, or in some other cases a multiple of these weights (see the remarks upon the atomic weight of iron, p. 102). The atomic weights thus obtained from the molecular weights are printed in large figures.

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[1] Abridged from a more complete table which I have given in my *Leçons de Philosophie chimique*, 1864. Hachette.

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[1] I have followed the example of Lothar Meyer in adding this column.

Names of Bodies	Formulæ		Densities referred to Air	Double Densities referred to Hydrogen (Weight of 2 vol.)	Molecular Weights	Composition of the Molecule
Water	H_2O	= 2 vol.	0·6235	18	18	**16** of oxygen 2 of hydrogen
Hydrogen sulphide . .	H_2S	= 2 vol.	1·1912	34·4	34	**32** of sulphur 2 of hydrogen
Sulphur dioxide . .	SO_2	= 2 vol.	2·247	64·9	64	**32** of sulphur 32 = 2 × 16 of oxygen
Sulphuric anhydride .	SO_3	= 2 vol.	2·763	79·8	80	**32** of sulphur 48 = 3 × 16 of oxygen
Selenious anhydride .	SeO_2	= 2 vol.	4·03	116	111	**79** of selenium 32 = 2 × 16 of oxygen
Hydrochloric acid . .	HCl	= 2 vol.	1·247	36	36·5	**35·5** of chlorine 1 of hydrogen
Methyl chloride . .	CH_3Cl	= 2 vol.	1·736	50·1	50·5	**35·5** of chlorine 12 of carbon 3 = 3 × 1 of hydrogen
Methyl bromide . .	CH_3Br	= 2 vol.	3·253	93·9	95	**80** of bromine 12 of carbon 3 = 3 × 1 of hydrogen
Hydriodic acid . .	HI	= 2 vol.	4·443	128	128	**127** of iodine 1 of hydrogen
Methyl iodide . . .	CH_3I	= 2 vol.	4·883	141	142	**127** of iodine 12 of carbon 3 = 3 × 1 of hydrogen

Methyl fluoride . .	CH_3F	= 2 vol.	1·186	34·3	34·1	**19·1** of fluorine 12 of carbon 3 = 3 × 1 of hydrogen
Nitrogen protoxide . .	N_2O	= 2 vol.	1·527	44·1	44	28 = 2 × **14** of nitrogen 16 of oxygen
Nitrogen dioxide . .	NO	= 2 vol.	1·038	29·98	30	**14** of nitrogen 16 of oxygen
Ammonia	NH_3	= 2 vol.	0·591	17·07	17	**14** of nitrogen 3 = 3 × 1 of hydrogen
Methylamine . . .	CH_5N	= 2 vol.	1·08	31·19	31	**14** of nitrogen 12 of carbon 5 = 5 × 1 of hydrogen
Phosphine . . .	PH_3	= 2 vol.	1·184	34·2	34	**31** of phosphorus 3 = 3 × 1 of hydrogen
Phosphorus trichloride .	PCl_3	= 2 vol.	4·742	136·9	137·5	**31** of phosphorus 106·5 = 3 × 35·5 of chlorine
Phosphorus oxychloride .	$POCl_3$	= 2 vol.	5·3	153·1	153·5	**31** of phosphorus 16 of oxygen 106·5 = 3 × 35·5 of chlorine
Arsine	AsH_3	= 2 vol.	2·695	77·8	78	**75** of arsenic 3 = 3 × 1 of hydrogen
Arsenic chloride . .	$AsCl_3$	= 2 vol.	6·3006	181·9	181·5	**75** of arsenic 106·5 = 3 × 35·5 of chlorine
Arsenic iodide . . .	AsI_3	= 2 vol.	16·15	464·9	456	**75** of arsenic 381 = 3 × 127 of arsenic
Triethylarsine . . .	$(C_2H_5)_3As$	= 2 vol.	4·61	162	162	**75** of arsenic 72 = 6 × 12 of carbon 15 = 15 × 1 of hydrogen
Marsh gas . . .	CH_4	= 2 vol.	0·559	16·1	16	**12** of carbon 4 = 4 × 1 of hydrogen

Names of Bodies	Formulæ	Densities referred to Air	Double Densities referred to Hydrogen (Weight of 2 vol.)	Molecular Weights	Composition of the Molecule
Carbon tetrachloride . .	CCl_4 = 2 vol.	5·415	156·4	154	**12** of carbon 142 = 4 × 35·5 of chlorine
Carbon protoxide . .	CO = 2 vol.	0·967	27·9	28	**12** of carbon 16 of oxygen
Carbon dioxide . .	CO_2 = 2 vol.	1·529	44·1	44	**12** of carbon 32 = 2 × 16 of oxygen
Carbon oxychloride . .	$COCl_2$ = 2 vol.	3·399	98·2	99	**12** of carbon 16 of oxygen 71 = 2 × 35·5 of chlorine
Carbon disulphide . .	CS_2 = 2 vol.	2·645	76·4	76	**12** of carbon 64 = 2 × 32 of sulphur
Silicon chloride . .	$SiCl_4$ = 2 vol.	5·939	171·5	170	**28** of silicon 142 = 4 × 35·5 of chlorine
Silicon fluoride . .	SiF_4 = 2 vol.	3·57	103	104·4	**28** of silicon 76·4 = 4 × 19·1 of fluorine
Silicon ethide . . .	$Si(C_2H_5)_4$ = 2 vol.	5·13	148·1	144	**28** of silicon 96 = 8 × 12 of carbon 20 = 20 × 1 of hydrogen
Stannic chloride . .	$SnCl_4$ = 2 vol.	9·199	265·7	259·8	**117·8** of tin 142 = 4 × 35·5 of chlorine
Stannic ethide. . .	$Sn(C_2H_5)_4$ = 2 vol.	8·021	231·6	233·8	**117·8** of tin 96 = 8 × 12 of carbon 20 = 20 × 1of hydrogen

Stannic dimethide-diethide	$Sn\left\{\begin{matrix}(CH_3)_2\\(C_2H_5)_2\end{matrix}\right\}$	= 2 vol.	6·838	197·5	205·8	**117·8** of tin 72 = 6 × 12 of carbon 16 = 16 × 1 of hydrogen
Zirconium chloride . .	$ZrCl_4$	= 2 vol.	8·15	235·4	232	**90** of zirconium 142 = 4 × 35·5 of chlorine
Titanium chloride . .	$TiCl_4$	= 2 vol.	6·836	197·4	190	**48** of titanium 142 = 4 × 35·5 of chlorine
Boron chloride . . .	BCl_3	= 2 vol.	3·942	113·7	117·5	**11** of boron 106·5 = 3 × 35·5 of chlorine
Boron fluoride . . .	BF_3	= 2 vol.	2·312	66·8	68·3	**11** of boron 57·3 = 3 × 19·1 of fluorine
Boron bromide . .	BBr_3	= 2 vol.	8·78	253·5	251	**11** of boron 240 = 3 × 80 of bromine
Boron trimethide . .	$B(CH_3)_3$	= 2 vol.	1·93	55·7	56	**11** of boron 36 = 3 × 12 of carbon 9 = 9 × 1 of hydrogen
Antimony trichloride .	$SbCl_3$	= 2 vol.	7·8	225·3	228·5	**122** of antimony 106·5 = 3 × 35·5 of chlorine
Triethylstibine . .	$Sb(C_2H_5)_3$	= 2 vol.	7·23	208·8	209	**122** of antimony 72 = 6 × 12 of carbon 15 = 15 × 1 of hydrogen
Vanadium tetrachloride .	VCl_4	= 2 vol.	6·69	193	193·2	**51·2** of vanadium 142 = 4 × 35·5 of chlorine
Bismuth trichloride .	$BiCl_3$	= 2 vol.	11·35	327·8	316·5	**210** of bismuth 106·5 = 3 × 35·5 of chlorine
Chromium oxychloride .	CrO_2Cl_2	= 2 vol.	5·55	159	155·4	**52·4** of chromium 32 = 2 × 16 of oxygen 71 = 2 × 35·5 of chlorine
Molybdenum pentachloride	$MoCl_5$	= 2 vol.	9·46	273	273·3	**95·8** of molybdenum 177·5 = 5 × 35.5 of chlorine

Names of Bodies	Formulæ	Densities referred to Air	Double Densities referred to Hydrogen (Weight of 2 vol.)	Molecular Weights	Composition of the Molecule
Tungsten pentachloride .	WCl_5 = 2 vol.	12·7	366	361·5	**184** of tungsten 177·5 = 3 × 35·5 of chlorine
Tungsten hexachloride .	WCl_6 = 2 vol.	13·2	382	397	**184** of tungsten 213 = 6 × 35·5 of chlorine
Niobium pentachloride .	$NbCl_5$ = 2 vol.	9·6	277	271·5	**94** of niobium 177·5 = 5 × 35·5 of chlorine
Niobium oxychloride . .	$NbOCl_3$ = 2 vol.	7·88	228	216·5	**94** of niobium 16 of oxygen 106·5 = 3 × 35·5 of chlorine
Tantalum pentachloride .	$TaCl_5$ = 2 vol.	12·9	372	359·5	**182** of tantalum 177·5 = 5 × 35·5 of chlorine
Zinc ethyl	$Zn(C_2H_5)_2$ = 2 vol.	4·62	123	122·9	**64·9** of zinc 48 = 4 × 12 of carbon 10 = 10 × 1 of hydrogen
Zinc methyl . . .	$Zn(CH_3)_2$ = 2 vol.	3·29	95	94·9	**64·9** of zinc 24 = 2 × 12 of carbon 6 = 6 × 1 of hydrogen
Lead tetramethide . .	$Pb(CH_3)_4$ = 2 vol.	9·6	277·2	266·4	**206·4** of lead 48 = 4 × 12 of carbon 12 = 12 × 1 of hydrogen
Mercuric chloride . .	$HgCl_2$ = 2 vol.	9·8	283	271	**200** of mercury 71 = 2 × 35·5 of chlorine

Mercuric bromide . .	$HgBr_2$	= 2 vol.	12·16	351	360	**200** of mercury 160 = 2 × 80 of bromine
Mercuric iodide . . .	HgI_2	= 2 vol.	16·2	468	454	**200** of mercury 254 = 2 × 127 of iodine
Mercuric methide . .	$Hg(CH_3)_2$	= 2 vol.	8·29	239·4	230	**200** of mercury 24 = 2 × 12 of carbon 6 = 6 × 1 of hydrogen
Mercuric ethide . . .	$Hg(C_2H_5)_2$	= 2 vol.	9·97	287·8	258	**200** of mercury 48 = 4 × 12 of carbon 10 = 10 × 1 of hydrogen
Osmic acid	OsO_4	= 2 vol.	8·89	256·7	252·6	**198·6** of osmium 54 = 4 × 16 of oxygen
Aluminium chloride . .	Al_2Cl_6	= 2 vol.	9·36	270	268	55 = 2 × **27·5** of aluminium 213 = 6 × 35·5 of chlorine
Aluminium bromide . .	Al_2Br_6	= 2 vol.	18·62	537·7	535	55 = 2 × **27·5** of aluminium 480 = 6 × 80 of bromine
Aluminium iodide . .	Al_2I_6	= 2 vol.	27	779·8	817	55 = 2 × **27·5** of aluminium 762 = 2 × 126·85 of iodine
Ferric chloride . . .	Fe_2Cl_6	= 2 vol.	11·39	328·9	324·8	111·8 = 2 × **55·9** of iron 213 = 6 × 35·5 of chlorine

IV.

Apparent Exceptions to the Law of Avogadro and Ampère.

The above method of the determination of molecular weights is founded upon the principle that molecules occupy two volumes in the state of gas or vapour, an atom of hydrogen occupying one volume. Now, the densities of a number of vapours are at variance with this proposition. Thus, judging from their vapour densities taken at a sufficiently high temperature, the molecules of the following compounds would occupy four volumes instead of two:—Ammonium chloride and similar compounds, phosphonium iodide, sulphuric acid, phosphorus pentachloride, iodine trichloride, calomel, amylene hydrochloride and hydrobromide, chloral hydrate, &c. But we must endeavour to discover whether the vapours of the compounds in question are not decomposed at the temperatures to which they are raised in order to take their densities, a point to which H. Kopp, Kekulé, and Cannizzaro long ago drew attention. If this is the case, it is obvious that the densities determined at these temperatures do not refer to these compounds themselves, but to the mixture of the products of their decomposition.

Thus, for example, we should not be authorised in saying that the molecule of ammonium chloride occupies four volumes if it could be shown that at 360°— the temperature at which the density was taken—this molecule is entirely decomposed into two new molecules—hydrochloric acid gas and ammonia gas—which exist side by side in a state of mixture, each occupying two volumes.

It has been proved that this decomposition does take place in the case of some of the compounds mentioned above, and we propose to give, in some detail, the facts and arguments upon which this proof rests.

I. It is unmistakable in the case of amylene hydrobromide, $C_5H_{10}.HBr = C_5H_{11}Br$. At a temperature which is not more than 40° or 50° above its boiling point, the vapour of this body presents a density (5·2) which agrees with the normal condensation into two volumes, and this density is constant between 150° and 180°. But from 180° upwards it decreases by degrees till at 360° it has sunk to one-half. The vapour is, therefore, completely dissociated into amylene and hydrobromic acid gas, which recombine upon cooling. The same phenomena are observed in amylene hydrochloride. Nevertheless the *recomposition* of the dissociated elements is not complete, especially in the case of amylene hydrobromide, for, when the flasks are opened under mercury, there is always a residue of a certain quantity of acid gas, testifying to the dissociation which has taken place at a high temperature. There can be but one interpretation of this fact. Amylene hydrobromide cannot possess several vapour densities. The true vapour density of its molecule is that which indicates a condensation into two volumes. The other or halved density indicates a halving of its molecule, and is not a true vapour density. It represents a mixture of decomposition products, and is, as we say, an apparent or anomalous vapour density.

II. The case is the same with phosphorus pentachloride, PCl_5. It was generally thought a few years ago, upon the authority of some very accurate but wrongly interpreted experiments of Cahours, that the molecule of phosphorus pentachloride answered to a condensation of elements into three volumes ($H_2O = 2$ vol.) It is more correct to say that we have here a phenomenon of partial decomposition or *dissociation*, according to the beautiful conception of Sainte-Claire Deville, and that, at the temperature at which this vapour is partly dissociated, of the two molecules which occupy four volumes, one is still intact and occupies two volumes, while the other is entirely decomposed into phosphorus trichloride, PCl_3, and into chlorine, Cl_2, these products of decomposition occupying four volumes; hence the apparent condensation of two molecules into six volumes, or of one molecule into three volumes. Recent experiments have greatly strengthened this interpretation. The dissociation of phosphorus pentachloride has, in fact, been prevented by diffusing its vapour either into an atmosphere of phosphorus trichloride or into an atmosphere of chlorine. Thus the vapour of the pentachloride being formed in a saturated medium of one or other of its products of dissociation, the latter is retarded, the product having become more stable. We may conceive, in fact, that the pentachloride being dissociated into trichloride and chlorine by heat, the trichloride will have less tendency to separate from the chlorine in an atmosphere saturated with trichloride, and that, on the other hand, the chlorine will have less tendency to separate from the protochloride in an atmosphere already saturated with chlorine. Whether, therefore, we diffuse the vapour of the pentachloride into an atmosphere of the trichloride or into that of chlorine, we shall under either condition prevent the decomposition of the molecule of the pentachloride into the trichloride and chlorine, and shall find that in this case the vapour of the pentachloride presents the normal density. We are, therefore, authorised in forming the conclusion that the molecule of this body offers, under these conditions, the normal condensation into two volumes. This also applies to phosphorus pentafluoride, PFl_5 = two volumes, which is gaseous at the ordinary temperature.

III. Nothing of this kind is to be observed in other compounds, such as phosphorus bromochloride, sal ammoniac, and sulphuric acid. At temperatures at which their vapours are formed, their molecules are, if not entirely, at least to a great extent dissociated; and in confirmation of the statement physical proofs may be brought forward from experiments upon diffusive power, refractive index, coloration, and the absorbing power for calorific and luminous rays. Thus Wanklyn and Erlenmeyer have shown that when the vapour of sulphuric acid, dissociated into anhydrous acid and water, is diffused through a tube drawn out to a capillary point, the aqueous vapour, being much less dense than that of the sulphuric anhydride, escapes more easily and in a larger quantity. Sainte-Claire Deville has, again, made an interesting experiment with phosphorus bromochloride, PCl_3Br_2, which is formed by the combination of bromine with phosphorus trichloride, thus corresponding with the pentachloride. The colour of its vapour was red, thus showing that it contained bromine. A similar observation had been made by the same author upon the dissociated vapour of the pentachloride, which showed the colour of chlorine. In the same manner we should be able to determine the absorption bands of the vapour of phosphorus pentachloride, which should contain those of chlorine.

IV. An argument of a different kind, but still of a physical nature, proves the dissociation of ammonium chloride; Marignac established this fact by showing that the quantity of heat necessary for the reduction of sal ammoniac into vapour is altogether out of proportion with the mean heat required for volatilisation, and strikingly equal to that which is produced by the combination of its elements, hydrochloric acid gas and ammonia.

V. Ammonium sulphydrate, NH_4HS, also does not exist undecomposed in a state of vapour. This vapour is really a mixture of hydrogen sulphide and ammonia in equal volumes, and it appears from Horstmann's[1] experiments, recently confirmed by Salet, that no contraction is observable when ammonia is mixed with hydrogen sulphide in any proportions between the temperatures of 60° and 86°. The assertion of Sainte-Claire Deville and Troost that two volumes of ammonia and one volume of hydrogen sulphide are condensed to two volumes is, therefore, without foundation.

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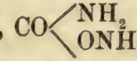
[1] A. Horstmann, *Annalen der Chemie u. Pharm.*, T. Supplement-Band vi. p. 74.

The body generally known as anhydrous carbonate of ammonia contains the elements $CO_2 + 2NH_3$. It is ammonium carbamate,  $CO\left\langle\begin{matrix}NH_2\\ ONH_4\end{matrix}\right.$. A. Naumann[1] has shown that its vapour forms six volumes, a mixture of two volumes of carbon dioxide and four volumes of ammonia.

VI. Let us pass to another body, calomel. From its vapour density we should assign to it the molecular weight 235·5 and the formula HgCl, but from other chemical considerations the double formula Hg_2Cl_2 appears more probable. It corresponds to mercurous oxide, Hg_2O. Hence we must admit that the vapour of calomel is dissociated at the high temperature at which its density is taken. And the chemical reactions of calomel render this dissociation very probable. It is well known how easily it decomposes in presence of the alkaline chlorides or iodides into mercuric chloride, $HgCl_2$, and mercury, Hg, a decomposition which is most accurately represented by the formula Hg_2Cl_2.

The fact of the dissociation of calomel vapour or mercurous chloride into mercuric chloride and metallic mercury has been demonstrated by Erlenmeyer and A. Le Bel. In contact with a platinum tube cooled by a current of cold water the vapour deposits metallic mercury upon the tube.

VII. As we have remarked above, chloral hydrate, $C_2HCl_3O.H_2O$, a very definite compound, seems also to form an exception to the law of Avogadro and Ampère. Its molecule, reduced to vapour, occupies four volumes, referred to an atom of hydrogen as occupying one volume. But at the temperature at which it is formed this vapour is entirely dissociated into a mixture of anhydrous chloral, C_2HCl_3O, and aqueous vapour, H_2O, the molecules of which each occupy two volumes. In the vapour of chloral hydrate the aqueous vapour is therefore free, and simply in a state of mixture with the vapour of the anhydrous chloral. The author proves this by making use of a method mentioned by Troost. This chemist heated crystallised potassium oxalate in the vapour of chloral to a temperature of 79°, working under such conditions that the tension of dissociation of the hydrated salt should be equal or a little inferior to the tension of aqueous vapour in the vapour of chloral hydrate, supposing that the latter were dissociated. Now, according to the principles developed by Sainte-Claire Deville and Debray, the dissociation of a body capable of forming a gaseous or volatile product ceases for a certain temperature, when this gaseous product or vapour has acquired, in the atmosphere in which it is formed, a certain tension, which is the tension of dissociation for that temperature. At 79° crystallised oxalate of potassium cannot, therefore, continue to produce aqueous vapour, when the atmosphere of chloral hydrate contains aqueous vapour under a tension which is equal or superior to that of the hydrated salt at 79°. Troost showed that, under these conditions, this salt emitted aqueous vapour, and therefore formed the conclusion that the vapour of chloral hydrate does not contain aqueous vapour in a state of mixture. The experiment was inaccurate and the conclusion inadmissible. The author has shown that crystallised potassium oxalate behaves in exactly the same manner when heated to 79° or 100°, either in an atmosphere of chloral hydrate or in a mixture of air and aqueous vapour, and that it does not produce water when in the two mixtures the aqueous vapour has the same tension, which tension is a little greater than the tension of dissociation of the hydrated salt. Indeed, anhydrous potassium oxalate can absorb a small quantity of aqueous vapour in an atmosphere of chloral hydrate, when the tension of the aqueous vapour present in this atmosphere is much greater than the tension of dissociation of the hydrated salt for the temperature at which we are working.

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[1] A. Naumann, *Annalen der Chemie u. Pharm.*, t. 160, p. 2.

These experiments leave no doubt as to the condition of the aqueous vapour in the vapour of chloral hydrate; it is simply in a state of mixture with the vapour of the anhydrous chloral. In fact, if we consider the decomposing action which is exercised by heat upon the greater number of chemical compounds, we shall not be astonished to find that in the compounds under discussion the point of decomposition is situated below the boiling point, or that the latter falls between the more or less restricted limits of temperature within which the compound suffers dissociation. Hydrochloric acid gas has undoubtedly a great affinity for ammonia at the ordinary temperature, but at 350° this affinity disappears or is very feeble, Marignac having shown that the combination between these two bodies cannot be effected at this temperature. Again, aniline and hydrochloric acid combine at ordinary temperatures.

accompanied by a large development of heat, but it has been shown that there is no development of heat when aniline and hydrochloric acid gas are brought in contact at a temperature of 230°.

It appears from the above discussion that the densities which correspond to four volumes of vapour refer to mixtures and not to intact compounds, and that the exceptions to the general proposition, that the molecules of compound bodies represent a condensation of their elements into two volumes of vapour, are more apparent than real.

V.

Atomic Constitution of Elementary Bodies in a State of Gas or Vapour.

The law of Avogadro and Ampère not only applies to the molecules of compound bodies, but also to the gases and vapours of elementary bodies. It is now admitted that the latter are formed of more or less complex molecules, and that, in the state of gas, these molecules, which are contained in equal numbers in equal volumes, are situated at immense distances relatively to their dimensions, but appreciably constant for different gases or vapours. Again, heat, when acting upon these gases or vapours, produces in them almost precisely the same changes of volume for the same variations of temperature and pressure. We cannot here discuss how this idea was first introduced into science; its historical aspect will be noticed presently. We will now only remark that the hypothesis of Avogadro and Ampère includes all gases or vapours, whether elementary or compound; and if, following the proposition given above, which is the natural consequence of these ideas, we admit that the molecule of compound bodies occupies two volumes, an atom of hydrogen occupying one volume, we must also admit that the molecules of elementary bodies occupy two volumes. Thus a molecule of hydrogen occupying two volumes will consist of two atoms, which is also the case with oxygen, nitrogen, chlorine, bromine, and iodine.

All these atoms are *diatomic*,[1] and here we again meet with the distinction which Gmelin had already established between the constitution of the gases or vapours of different elementary bodies. This distinction has now acquired great importance.

Ozone is, as we all know, condensed oxygen; this has been proved by the experiments of Andrews and Tait, and especially by the ingenious and careful researches of Soret: but ozone is an element, and since three volumes of oxygen are condensed into two volumes of ozone, which represent a molecule, O_3, we may say that ozone is triatomic.

When heated to 500° the vapour of sulphur is still more powerfully, though similarly, condensed; it becomes hexatomic, six atoms of sulphur being condensed into two volumes—that is to say, into one molecule—of this vapour. Here, therefore, between these two simple bodies, oxygen and sulphur, so similar in their chemical functions, we have an analogy which deserves our attention. Both are capable of condensation, and heat destroys this state of condensation. Ozone, when heated, gives oxygen, and the molecule of condensed sulphur, S_6, is in a manner decomposed at a temperature of 1,000°, and forms three molecules of vapour of ordinary sulphur, S_2, which is diatomic.

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[1] The term diatomic molecules clearly and correctly expresses molecules formed of two atoms; but it is clear that this definition of atomicity differs widely from that which is generally attributed to it, i.e. the equivalence or valency of atoms.

The vapours of phosphorus and arsenic are examples of a different state of condensation; their density, compared with that of hydrogen, is 62 for phosphorus and 150 for arsenic. Two volumes of phosphorus vapour contain, therefore, 124 parts of phosphorus—that is to say, four atoms—and two volumes of arsenic vapour contain 300 parts of arsenic, also four atoms. Both vapours are tetratomic, or, in other words, the molecules of phosphorus and arsenic are formed of four atoms. Now, it has been ascertained that this atomic grouping cannot be destroyed by heat, at least not within the limits of temperature at which experiments have as yet been conducted; but this fact does not justify the conclusion that it would resist the most powerful action of heat which could be produced or conceived, for it is very possible that the atoms in question would separate if exposed to the temperatures at which iron and platinum melt, and which are certainly not so high as those present in the sun. What, therefore, it may be remarked in passing, is the chemistry possible at the solar temperature? It is doubtless very simple and certainly very different from terrestrial chemistry. Not to mention the difference of elements, can we be sure that known elementary bodies can enter into combination at the solar temperature, or that they produce in other worlds the same compounds as upon the earth? That is a matter of temperature.

To return to the question before us, we now come to the simplest of all the molecular groups—that, namely, of mercury, cadmium, and probably other bivalent metals. The vapour density of mercury is 100, hydrogen being taken as unity; but the atomic weight of mercury, calculated from the density of volatile mercuric compounds (see p. 109), as well as from the law of Dulong and Petit, is 200. It follows that a molecule of mercury which occupies two volumes contains only one atom of mercury. The vapour of mercury is monatomic. The molecule and the atom of mercury are identical, and this consequence of the law of Avogadro and Ampère, and which till now has been nothing more than a theoretical suggestion, has been recently confirmed by the researches of Kundt and Warburg, the principle and results of which we shall now proceed briefly to describe.

It is generally known that the specific heat of gases is greater when they are heated under constant pressure, and with freedom to expand, than when they are heated under constant volume with increase of pressure; for it is evident that, in the first case, the gas must be provided not only with the heat necessary to raise its temperature—that is to say, to augment the mean *vis viva* of its molecules—but also that which is absorbed to perform a certain external work, which would correspond to the displacement of an elastic envelope, supposing the gaseous volume to be thus limited. This mechanical work is not performed when the expansion is prevented ; therefore less heat is absorbed by the gas during the elevation of its temperature. It has even been calculated, from the mechanical theory of heat, what the relation should be between the capacity of gases under constant pressure and the capacity under constant volume. According to Clausius, this theoretical relation is 1·67. Now, it appears that for elementary gases, such as hydrogen, oxygen, nitrogen, &c., this relation is smaller than that indicated by the theory (about 1·4). The explanation of this is, that these gases, which are diatomic, absorb a certain quantity of heat when they are heated under constant volume, not for the performance of external work, as there is no expansion, but to perform certain work in the molecule itself, which is formed of two atoms.

Now, Kundt and Warburg have shown that this internal work is not performed in the case of mercury vapour,[1] and that the relation between the specific heats of mercury vapour under constant pressure and under constant volume is the same as that indicated by theory. It is obvious that in this case there is no internal work, because the molecule is only composed of a single atom.

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[1] Kundt and Warburg have calculated the relation of the two specific heats from the velocity of the propagation of sound in mercury vapour. The calculation was made from the length of a sound-wave. In determining the length of a given sound-wave in the air and in mercury vapour, they found that the relation of the two specific heats of mercury vapour was $\frac{C}{c} = 1{\cdot}67$. (*Berichte der Deutschen Chem. Gesellsch. zu Berlin*, 1875, t. viii. p. 945. Pogg., *Ann.*, t. clvii. p. 353.)

If similar experiments were undertaken for the vapours of sulphur, phosphorus, and arsenic, the result would doubtless be very different. Here the internal work should be considerable, and the relation between the specific heats under constant pressure and under constant volume would be still smaller than for the diatomic gases.

The distinction which it has been necessary to establish between the molecular constitution of the different elementary bodies in the gaseous state has now been explained, and the significance and value of the results given on p. 70 made intelligible.

VI.

The New System of Atomic Weights is in Harmony with the Law of Dulong and Petit.

There is not a single exception to the law of Dulong and Petit, as a glance at the following table will show. The second column of this table gives the specific heats of the elementary solid bodies mentioned in the first. The third column gives the atomic weights; the fourth, the product of the atomic weights multiplied by the specific heats. These products may be termed atomic heats, for they represent the quantities of heat absorbed by the atoms when their temperature is raised one degree. We see that these atomic heats are appreciably constant. This constitutes the great physical law discovered by Dulong and Petit.

Names of Elementary Bodies	Specific Heats	Atomic Weights	Products of the Atomic Weights by the Specific Heats
Aluminium	0·2143	27·5	5·5
Antimony	0·0523	122	6·4
Arsenic (crystallised)	0·0830	75	6·2
Bismuth	0·0305	210	6·5
Boron (crystallised) at 233°	0·366	11	(4)
at 600°	0·5 (?)	11	5·5
Bromine (solid)	0·0843	80	6·7
Cadmium	0·0567	112	6·3
Carbon diamond at 985°	0·459	12	5·5
graphite at 978°	0·457	12	5·5
Cobalt	0·1067	58·6	6·3
Copper	0·0952	63·3	6·1
Gold	0·0324	196·2	6·4
Indium	0·0570	113·4	6·5
Iodine	0·0541	126·85	6·8
Iridium	0·0326	196·7	6·4
Iron	0·1138	55·9	6·4
Lead	0·0314	206·4	6·5
Lithium	0·9408	7	6·6
Magnesium	0·2499	24	5·9
Manganese	0·1217	55	6·7
Mercury (solid) at − 59°	0·0319	200	6·4
Molybdenum	0·0722	96	6·9
Nickel	0·107	58·6	6.3
Osmium	0·0311	198·6	6·2
Palladium	0·0591	106·2	6·3
Phosphorus (ordinary) at 19°	0·189	31	5·9
Platinum	0·0324	196·7	6·4
Potassium	0·1655	39·137	6·5
Rhodium	0·0580	104·1	6
Ruthenium	0·0611	103·5	6·3
Selenium	0·0762	79	5·9
Silicon at 232°	0·202	28	5·7
Silver	0·0570	108	6·1
Sodium	0·2934	23·043	6·7
Sulphur	0·1776	32·075	5·8
Tellurium	0·0474	128	6·1
Thallium	0·0336	203·6	6·8
Tin	0·0548	118	6·5
Tungsten	0·0334	184	6·1
Zinc	0·0955	64·9	6·2

The mean of the atomic heats of solid elementary bodies is 6·4, and the extreme limits within which these atomic heats vary are comprised within the numbers 5·5 and 6·9. The elements whose atomic heats are a little too low are certain metalloids of small atomic weight, such as boron, silicon, carbon, phosphorus, arsenic, sulphur, and selenium, to which must be added aluminium. Those whose atomic heat exceeds the average are certain metals, amongst which must be mentioned lithium, sodium, potassium, thallium, calcium, manganese, molybdenum, &c., to which we must add iodine and bromine. But is it not a fact of some importance that while the atomic weights vary in the proportion of 1 to 30, and the specific heats in the proportion of 1 to 7, the products of these two quantities—that is to say, the atomic heats—only vary in the proportion of 1 to 1·2?

The variations of atomic heats may be attributed to various causes. In the first place, to errors of observation connected with the determination of atomic weights, and also with that of specific heats. Some of these determinations relate to bodies which have not yet been obtained in a state of perfect purity. On the other hand, as Regnault observes,[1] the determination—and, we may add, the notion—of specific heats includes some uncertainties, 'for it includes several elements which we have not as yet been able to eliminate, especially the latent heat of dilatation, and a portion of the latent heat of fusion, which is gradually absorbed by bodies, as they frequently soften long before the temperature which is regarded as their melting point is reached. Thus the heat applied to a solid body not only serves to raise its temperature—that is to say, to augment the vibratory energy of its molecules—but a portion, perhaps a considerable portion, of this heat is employed in performing the work of expansion, which work prepares the way for a change of state by diminishing the force of cohesion, by affecting the disaggregation of molecules, or by determining modifications of texture. All these changes give rise to thermal phenomena, which are in some manner superposed, and the sum of which constitutes what is called specific heat. It is impossible to distinguish the part played by each of these elements in the phenomenon; but it is surely remarkable that, in spite of the complexity of the phenomena, so simple and so great a law should be evolved from them when formulated in the terms employed by Dulong and Petit. Doubtless it is not rigorously exact, but the different elements of which specific heat is composed obviously cannot act exactly in the same manner, either in different elements or in the same element at different temperatures; and yet these several influences enable us to estimate the variations to which specific heat is subject, and consequently the atomic heat of certain bodies according to the temperature. It is probable that for every element there are limits of temperature within which the specific heat is almost constant; experiment at least has proved it to be so in the case of certain metals, such as iron, copper, zinc, silver, antimony, mercury, platinum, lead, and bismuth, and it is to be noticed that the atomic heats of these metals approach very closely to the average 6·4. May we not conclude from this fact that if the limits of temperature within which the specific heat was appreciably constant were known for every element, the atomic heats calculated from specific heats thus determined would more nearly approach the average 6·4? If this were so the law of Dulong and Petit, which is only an approximate one—as, indeed, are all physical laws, especially the law of Marriotte—would acquire a greater degree of accuracy.

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[1] *Annales de Chimie et de Physique*, 3e série, t. xxvi. p. 262. 1849

However this may be, the variations in specific heat are considerable for the three elements which alone seemed to form an exception to the law of Dulong and Petit—carbon, boron, and silicon. These exceptions have just disappeared, for it appears, from the investigations of Weber, that the specific heat of carbon, boron, and silicon increases with the temperature, and becomes constant at high temperatures. This fact has been proved in the case of carbon and silicon, and it has become very probable in that of boron.

The specific heat of the diamond is very nearly 0·4589, that of graphite 0·4670; for silicon it is 0·2029 between 0° and 252°·3; for boron it varies from 0·1915 to 0·3663 between −79° and 263°·6. Weber admits, without, however, giving any proof, that it is nearly 0·5 at higher temperatures. If the specific heats thus corrected are multiplied by the atomic weights of the three elements in question, we obtain for their atomic heats numbers which approximate to the average 6·4.

——	Carbon	Silicon	Boron
Specific heats . . .	0·467	0·203	0·5 (?)
Atomic weights . . .	12	28	11
" heats . . .	5·6	5·7	5·5

What explanation can be given of the fact that the atomic heat of carbon, boron, and silicon, at low temperatures, is so far below that of the other solid elements? The following consideration will give a clue to the interpretation. In order to raise the atomic heat of these three elements to the level of that of the other solid elements, it would be necessary to multiply their specific heat at low temperatures by far higher numbers than their true atomic weights; thus, in the case of the diamond, it would be necessary to multiply its specific heat by 48—that is to say, by the weight of four atoms of carbon—before we could obtain a result at all in accordance with those given by the other solid elements. Can it be that this is the atomic weight of diamond, and that heat, in acting upon this body, sets in motion aggregates of atoms, condensed atoms, instead of acting upon isolated atoms? The same question arises in the case of graphite. To make its atomic heat equal the product 6·6, it is necessary to multiply its specific heat at low temperatures—that is to say, at 200°—by 33. This product 6·6 would represent the atomic heat of graphite, if 33 expressed its atomic weight. By a coincidence, which can scarcely be attributed to chance, this number 33 has been considered by Brodie as the true atomic weight of graphite, which forms, according to this chemist, a curious compound with oxygen, in which it has the atomic weight 33. This compound of graphite has been called graphitic acid.[1] Similar considerations apply also to boron and silicon; they are, however, of little importance, since these elements, from the researches of Weber, are now included in the general rule.

Thus, if the atomic weights given in the table upon p. 124 are adopted, there are now no exceptions to the law of Dulong and Petit, which is the strongest argument we can invoke in favour of the new system of atomic weights.

There is an important fact which should be noticed before quitting this subject. The law of specific heats only applies to solid bodies. Bromine in a solid state conforms to it, but no longer does so when liquid, for after liquefaction its specific heat is considerably augmented. This is generally true for liquids. It is well known that the specific heat of water is twice that of ice; that of liquid mercury is also higher than that of solid mercury, but here the difference is so slight (0·0333 and 0·0325) that it does not sensibly affect the value of the atomic heat. The state of aggregation exercises, therefore, a certain influence upon the absorption of heat by the atoms of a body. This influence is well marked in the gases; and on this point we will only notice one important fact—that the atomic heat of the elementary diatomic gases, hydrogen, oxygen, nitrogen, and chlorine, is sensibly half the atomic heats of the solid elements.[1] This is evident from the following table :—

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[1] It is well known that in treating graphite with nitric acid and potassium chlorate Brodie obtained a curious acid—graphitic acid—in which he admits the existence, not of carbon, but of graphite as such. He represents the composition of this acid by the formula $Gr_4H_4O_5$, in which the atomic weight of graphite is the same as its thermal equivalent, 33.

—	Specific Heats under Constant Pressure	Atomic Weights	Products
Hydrogen	3·4090	1	3·409
Oxygen	0·2175	16	3·286
Nitrogen	0·2438	14	3·413
Chlorine	0·1210	35·5	4·295

To obtain the double products, the specific heats must be multiplied by doubled atomic weights—that is to say, by the molecular weights.

Molecular Heats.—It has been admitted as a general rule that equivalent quantities of compound bodies possessing a similar atomic composition possess also the same specific heat. The products of the specific heats of these bodies by their molecular weights are sensibly equal, and if this product is called the 'molecular heat'

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[1] It is a fact worthy of notice that if the atomic heat of hydrogen and oxygen is calculated from the molecular heat of water (in the state of ice) the values obtained will be sensibly equal to those calculated from the specific heat of gaseous hydrogen and oxygen. In fact, according to the law of Hermann Kopp and Woestyn (p. 132), the molecular heat of water, which contains three atoms, should equal the sum of the atomic heats of these three atoms, and the quotient of this molecular heat by 3 should represent the atomic heat of hydrogen and oxygen. Now, the specific heat of ice being 0·5,

$$\frac{0{\cdot}5 \times 18}{3} = \frac{9}{3} = 3.$$

If, on the contrary, the atomic heat of the elements of water is calculated from the specific heat of liquid water, a double value (6) is naturally found, which approximates to the mean of the atomic heats of the solid elements (6·4).

we may say that such bodies possess the same molecular heat, or, in other words, that their molecules absorb the same quantity of heat when their temperature is raised one degree.[1]

As Hermann Kopp has remarked, this law has been verified in a great number of cases; thus the nitrates and the chlorates NO_3R', ClO_3R', the metaphosphates and the metarsenates PO_3R' and AsO_3R', which present a similar composition, possess sensibly the same molecular heat.[2] This is also true for the perchlorates and permanganates ClO_4R', MnO_4R', the sulphates and the chromates SO_4M'' and CrO_4M'', the carbonates CO_3M'', and the metasilicates SiO_3M''. The law in question appears to be a result of the law of Dulong and Petit, according to which the atoms of elementary solid bodies require the same quantity of heat to produce a given increase in their vibratory energy. Hence similar compounds containing the same number of atoms must be furnished with the same quantities of heat to produce a given increase in the vibratory energy of all these atoms. Hence, again, the molecular heat must increase with the number of atoms of which the molecule is composed. This agrees with observation. Upon comparing the molecular heats of a great number of compounds, we find that they consist of the sum of the atomic heats of the elements. In fact, the products of the specific heats of the molecular weights will at once be seen to be equal to as many times 6·4 (mean of atomic heats) as the compound body contains elementary atoms. Expressing the product in question as C M, then

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[1] M. Regnault has expressed this law in the following manner:—The specific heats of compound bodies, possessing similar chemical formulæ, are inversely proportionate to their 'equivalents.' (*Ann. de Chim. et de Phys.*, 3^e série, t. xxvi. p. 264.)

[2] The molecular heat of the nitrates is a little lower than that of the chlorates, the metaphosphates, and the metarsenates, a circumstance which tends to prove that the atomic heat of nitrogen is sensibly below the average.

$$\mathrm{C\,M} = n \times 6{\cdot}4.$$[1]

This relation is true for a great number of bodies, principally for the chlorides, bromides, iodides, even for the complex double chlorides, containing seven or even nine elementary atoms,[2] such as ZnK_2Cl_4 and PtK_2Cl_6. In some cases it may be used as an indirect verification of atomic weights. Thus Regnault observed some time ago that the molecular heat of the chlorides of tin, titanium, and silicon is sensibly the same, on condition

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[1] Hermann Kopp, *Comptes rendus*, t. lvi. p. 1254. Woestyn has stated the law of the specific heats of compound bodies in a general manner by saying that the atom of the element preserves its own specific heat in the compound into which it enters. If, therefore, we represent the atomic weights of several simple bodies by p, p', p'', and their specific heats by c, c', c'', the products, $pc, p'c', p''c''$, will express their atomic heats. Let C represent the specific heat of a compound formed of a certain number n, n', n'' of atoms p, p', p'', the molecular heat C M of this composition will be

$$\mathrm{C\,M} = n\,p\,c + n'\,p'\,c' + n''\,p''\,c'' + \ldots$$

and as by the law of Dulong and Petit $p\,c = p'\,c' = p''\,c''$, then

$$\mathrm{C\,M} = (n + n' + n'' + \ldots)\,p\,c,$$

$p\,c$ being equal to 6·4. This statement expresses the same proposition as that given in the text after H. Kopp.

[2] There are, however, some exceptions relative to certain metallic sulphides and oxides. (H. Kopp.)

that they are represented by similar formulæ RCl_4, in which $n=5$; thus:—

——	Specific Heats	Molecular Weights	Products. (Molecular Heats)
Chloride of tin . . .	0·1413	260	36·7
„ titanium . .	0·1813	190	34·8
„ silicon . .	0·1907	170	32·4

We see that the products (C M) are sensibly equal, which is an argument in favour of the molecular weight 170 for chloride of silicon, $SiCl_4$, and consequently of the atomic weight 28 for silicon.

The law of H. Kopp and Woestyn, which has been illustrated above, may be said to furnish in a great number of cases the means of calculating the atomic heat of elements from the molecular heat of their compounds. For example, according to Regnault, the specific heats of chloride. bromide, and iodide of lead are as follows: 0·0664, 0·0533, 0·0427. If these numbers are multiplied by the molecular weights 277·4, 366·2, 460·1 of the three compounds in which we suppose $n=3$, we obtain the products—

$PbCl_2$	18·4
$PbBr_2$	19·5
PbI_2	19·6.

Subtracting from these three products the atomic heat of lead, 6·5, we obtain 11·9, 13, 13·1, which represent the calorific capacities of the two atoms of chlorine, bromine, and iodine contained in the chloride, iodide, and bromide of lead. The half of these numbers, 5·9, 6·5, 6·55, represents, therefore, the atomic heat of chlorine, iodine, and bromine, and we see at once how closely the atomic heat of the chlorine contained in a solid chloride approximates to the average 6·4; and this seems to be a legitimate conclusion, since the composition of chloride of lead is unquestionably the same as the bromide and iodide. Finally, the agreement which we have proved to exist between the calculated atomic heats and those deduced from direct observation for Br and I would not hold if we were to adopt another hypothesis for the constitution of the compounds in question—for example, if we assumed $n=2$. This point will be developed presently.

We must add that Regnault was able to deduce the atomic heat of the alkaline metals, potassium, sodium, and lithium, from the calorific capacity of their compounds, and that the values thus calculated are found to agree with the results of experiments afterwards made with the isolated metals.

It should also be remarked that the thermal equivalents of the metals as deduced by Regnault from their specific heats are the same as our atomic weights, and that this distinguished physicist has long recognised the great importance of the law of Dulong and Petit in the determination of atomic weights.[1]

We will take one more example in illustration of the subject now before us.

Is the atomic weight of mercury 100 or 200? In the first case, if we represent 100 parts of mercury by *Hg*, then the mercurous and mercuric chlorides, bromides, and iodides must be represented by the following formulæ :—

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[1] See the note on p. 140.

Mercurous Compounds.	Mercuric Compounds.
$\mathit{Hg}_2\mathrm{Cl}$	$\mathit{Hg}\mathrm{Cl}$
$\mathit{Hg}_2\mathrm{Br}$	$\mathit{Hg}\mathrm{Br}$
$\mathit{Hg}_2\mathrm{I}$	$\mathit{Hg}\mathrm{I}$.

If, however, we represent 200 parts of mercury by the symbol Hg, they become—

Mercurous Compounds.	Mercuric Compounds.
$\mathrm{Hg_2Cl_2}$	$\mathrm{HgCl_2}$
$\mathrm{Hg_2B_2}$	$\mathrm{HgBr_2}$
$\mathrm{Hg_2I_2}$	$\mathrm{HgI_2}$

Judging from the specific heats of these compounds, the latter system of formulæ is to be preferred. In fact, if we take 200 as the atomic weight of mercury, then in mercurous compounds $n=4$, and in mercuric compounds $n=3$, and the molecular heats which may be calculated from the formula $\mathrm{C\,M} = n \times 6{\cdot}4$ are sensibly equal to those which are directly deduced from the specific heats obtained by experiment.

Formulæ	Specific Heats	Molecular Weights. Hg = 200	Products of Specific Heats by Molecular Weights. Observed Molecular Heats	Calculated Molecular Heats. $n \times 6{\cdot}4$
$\mathrm{HgCl_2}$	0·0689	271	18·67	19·2
$\mathrm{HgI_2}$	0·0420	454	19·06	19·2
$\mathrm{Hg_2Cl_2}$	0·05205	471	24·51	25·6
$\mathrm{Hg_2I_2}$	0·0385	654	25·18	25·6

The resemblance is here very striking between the calculated values and those obtained by experiment. This would no longer be the case if the first system of formulæ were adopted, and $n=3$ represented the mercurous and $n=2$ the mercuric compounds.

Formulæ	Specific Heats	Equivalents. Hg = 100	Products of the Specific Heats by the Equivalents. Observed Molecular Heats	Calculated Heats of the Equivalents. $n \times 3{\cdot}2$
$HgCl$	0·0689	135·5	9·33	6·4
HgI	0·0420	227	9·53	6·4
Hg_2Cl	0·05205	235·5	12·25	9·6
Hg_2I	0·0385	327	12·59	9·6

We may close this subject with the following remark:—If the considerations drawn from the specific heats of the chlorides and bromides of mercury are such as to influence our choice between the numbers 100 and 200 for the atomic weight of mercury, it is clear, on the other hand, that they throw no light upon the question as to whether or not the formulæ of mercurous compounds should be doubled. Cannizzaro prefers the simple formula HgCl to Hg_2Cl_2, because it agrees with the vapour density of calomel. We refuse to accept the latter formula, because the vapour of calomel presents an anomalous density (p. 115), and not from the considerations drawn from the specific heats; for, in doubling the formula, we multiply by 2 each member of the equation $\text{C M} = n \times 6{\cdot}4$, which, therefore, leaves the question proposed undecided. This is true in many other cases.

Molecular Volatilities.—Bunsen has discovered a curious relation between the molecular weights and the volatility of certain salts, especially the haloid salts. If equal weights (one centigramme, for example), of alkaline chlorides, bromides, or iodides are exposed in the hottest part of the same Bunsen burner, we shall find that under these conditions, when the amount of heat furnished in a given time is sensibly the same, these several salts take a very different length of time to volatilise, which is almost inversely proportional to their molecular weights, so that by multiplying the times of volatilisation by the molecular weights we obtain products which, though not identical, sensibly approximate to a mean value (4977). The following table gives, according to Bunsen, the times of volatilisation in seconds for one centigramme of various haloid salts. We have added the corresponding molecular weights, and the products of these weights by the times of volatilisation:—

Salts	Times of Volatilisation	Molecular Weights	Products
Cæsium chloride . . .	31·3	166	5258
Potassium iodide . . .	29·8	165	4934
Sodium chloride . . .	84·25	58 5	4929
Lithium chloride . . .	114·0	42·5	4845
Potassium chloride . . .	65·4	74·6	4879
Sodium bromide . . .	48·8	102·7	5012
Potassium bromide . .	41·6	118·8	4942
Rubidium chloride . .	38·6	120·7	4659
Sodium iodide . . .	35·7	149·5	5337
		Mean .	4977

We see that the products vary between the numbers 4659 and 5337—that is to say, in the proportion of 1 to 1·4—while the times of volatilisation vary from 29·8 to 114, in the proportion of 1 to 3·8. This result, though only approximate, is significant, and we must remember that the difficulties attending the experiment scarcely admit of greater accuracy. It shows that in an equally hot flame, and in a given time, the same number of molecules of the haloid salts are volatilised, or, in other words, that the *molecular volatilities* are the same.

VII.

The New System of Atomic Weights is in Harmony with the Law of Isomorphism.

The demonstration of this point will be neither long nor difficult. We have already observed (p. 60) the assistance which Berzelius derived from isomorphism in the determination of certain atomic weights, such as those of aluminium and iron. The principle which guided him in these considerations was correct. The atomic weights of simple bodies must be so determined that analogous and isomorphous compounds shall receive similar formulæ. This principle is respected by the new system of atomic weights.

We need not here enumerate all the cases of isomorphism presented by the combinations of analogous elements, and will therefore only mention the following:—the oxides,

$$As_2O_3, \qquad Sb_2O_3;$$

the sodium phosphates and arsenates,

$$PO_4.Na_2H + 12H_2O,$$
$$AsO_4.Na_2H + 12H_2O;$$

the corresponding ammonium salts,

$$PO_4.(NH_4)_2H,$$
$$AsO_4.(NH_4)_2H;$$

the sulpharsenite and sulphantimonite of silver,

AsS_3Ag_3,
SbS_3Ag_3;

and the isomorphous phosphates, arsenates, and vanadates of the apatite group—

$(PO_4)_3Ca_5Cl$ apatite,
$(PO_4)_3Pb_5Cl$ pyromorphite,
$(AsO_4)_3Pb_5Cl$ mimetesite,
$(VO_4)_3Pb_5Cl$ vanadinite.

We shall return to the latter compounds. Here we need only remark that since the researches of Roscoe the atomic weight of vanadium has been altered, so that vanadinite, which is isomorphous with apatite, is represented by a similar formula; secondly, that calcium and lead, bivalent metals in the new system of atomic weights, cannot be replaced in the isomorphous compounds under discussion by univalent metals, such as potassium or sodium.

The latter point is important and requires explanation. The law of isomorphism teaches us that the alkaline metals, amongst which we have included silver, because it also is univalent, form a separate group, distinctly separated from the several groups of bivalent metals, such as magnesium, calcium, barium, strontium, lead, &c. Thus the sulphate and selenate of silver,

SO_4Ag_2,
SeO_4Ag_2,

are isomorphous with the anhydrous sulphate and selenate of sodium,

SO_4Na_2,
SeO_4Na_2.

On the other hand, the alkaline sulphates, selenates, permanganates, and perchlorates are isomorphous with each other, but not with the corresponding salts of the magnesium series. Thus we have—

SO_4KH isomorphous with SeO_4KH (Mitscherlich),

$SO_4Na_2 + 10H_2O$ isomorphous with $\begin{cases} CrO_4Na_2 + 10H_2O, \\ SeO_4Na_2 + 10H_2O. \end{cases}$

The same remark applies to potassium perchlorate and permanganate, which, by the new system of atomic weights, are represented by similar formulæ—

ClO_4K potassium perchlorate,
MnO_4K potassium permanganate.

In the equivalent notation they were written—

$ClO_7.KO$ perchlorate of potash,
$Mn_2O_7.KO$ permanganate of potash.

The isomorphism of the chromates and manganates with the sulphates and selenates also deserves notice; it led Berzelius to halve the atomic weights which he had formerly attributed to chromium and manganese.

The isomorphism of the alkaline chlorides, bromides, iodides, and chloroplatinates is so well known that there is no occasion to lay stress upon it here. It is admitted that silver sulphide and cuprous sulphide[1] are isomorphous, at least in their compounds. These sulphides are represented by the following analogous atomic formulæ :—

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[1] The isomorphism of cuprous sulphide and silver sulphide suggested the following reflections to V. Regnault, which are given at p. 346 of vol. ii. of his *Cours élémentaire de Chimie*, 2nd edition:—'Native sulphide of silver is isomorphous with the native sub-sulphide of copper, Cu_2S; these two sulphides seem to have the power

Ag_2S silver sulphide,
Cu_2S cuprous sulphide ;

whilst in the equivalent notation they received the dissimilar formulæ—

of replacing each other in all proportions, as, for example, in the varieties of fahlerz. We have maintained that this isomorphism exists only between bodies possessing the same chemical formulæ, and we have frequently referred to this law in fixing the equivalents of elementary bodies. But sulphide of silver would form an exception to the law if we give it the formula AgS—that is to say, if we adopt the number 1350 as the equivalent of silver. This consideration has led several chemists to give to sulphide of silver the formula Ag_2S, and Ag_2O to protoxide of silver, and to take the number 675 as the equivalent of silver. This view has been confirmed by several other circumstances which demand our attention for a few moments. Physicists have shown by a great number of experiments that there exists a very simple relation between the specific heats of bodies and their chemical equivalents. This law states that *the specific heats of elementary bodies, within narrow limits, vary inversely as their equivalents.* Now, silver will only satisfy this law when the number 675 is received as its equivalent. Moreover, a law similar to that which we have just indicated for elements has been recognised for the specific heats of compounds. This law may be thus stated : *The specific heats of compounds possessing the same formula, within narrow limits, vary inversely as the numbers which represent the chemical equivalents of these compounds.* Now, the sulphides of silver and copper satisfy this law if we represent sulphide of silver by the formula Ag_2S.

'But if we write the formula of sulphide of silver Ag_2S, and consequently that of protoxide of silver Ag_2O, we must write the formula of soda Na_2O, and not NaO, as we have hitherto done, for we have seen that the sulphate of silver is isomorphous with the anhydrous sulphate of soda. The salts of potash and of lithia being isomorphous with the corresponding salts of soda, when they contain the same quantities of water of crystallisation, we must give to potash the formula K_2O and to lithia Li_2O,' &c.

AgS	sulphide of silver,
Cu_2S	sulphide of copper.

On the other hand, the metals, whose atomic weights have been doubled by Cannizzaro, present numerous cases of isomorphism, and form a group perfectly distinct from the preceding. The isomorphism of the nitrates of barium, strontium, and lead, which crystallise in octohedra, is well known, as also of the carbonates isomorphous with Iceland spar, which crystallise in rhombohedra.

CO_3Ca''	calcium carbonate (Iceland spar),
CO_3Mg''	magnesium carbonate (magnesite),
CO_3Mn''	manganous carbonate (diallogite),
CO_3Fe''	ferrous carbonate (siderite),
CO_3Zn''	zinc carbonate (smithsonite).

The clinorhombic sulphates and selenates of the magnesian series, which crystallise, some with seven, others with six, molecules of water, form two isomorphous groups—

First clinorhombic group .	$SO_4Fe'' + 7H_2O$	ferrous sulphate,
	$SO_4Co'' + 7H_2O$	cobalt sulphate,
	$SO_4Mn'' + 7H_2O$	manganouss ulphate,
	$SeO_4Fe'' + 7H_2O$	ferrous selenate.
Second clinorhombic group	$SO_4Mg'' + 6H_2O$	magnesium sulphate,
	$SO_4Ni'' + 6H_2O$	nickel sulphate,
	$SO_4Co'' + 6H_2O$	cobalt sulphate,
	$SO_4Zn'' + 6H_2O$	zinc sulphate,
	$SeO_4Ni'' + 6H_2O$	nickel selenate.

It is a curious fact that, under certain circumstances, these same sulphates and selenates can crystallise in orthorhombic prisms, and, according to Mitscherlich, the sulphates and selenates of nickel and the selenate of zinc (with seven molecules of water) in quadratic prisms: they are therefore isodimorphous.

We must further notice the isomorphous sulphates and selenates, which crystallise in the anorthic system with five molecules of water—

$SO_4Cu'' + 5H_2O$ copper sulphate,
$SeO_4Cu'' + 5H_2O$ copper selenate,
$SO_4Mn'' + 5H_2O$ manganous sulphate,
$SeO_4Fe'' + 5H_2O$ ferrous selenate.

Other isomorphous sulphates and selenates crystallise with four molecules of water in clinorhombic prisms—

$SO_4Mn'' + 4H_2O$ manganous sulphate,
$SeO_4Mn'' + 4H_2O$ manganous selenate,
$SO_4Fe'' + 4H_2O$ ferrous sulphate.

And, lastly, we must not forget, in the order of compounds now before us, the numerous double isomorphous sulphates of the magnesian series, $SO_4M''.SO_4R_2 + 6H_2O$, which crystallise in clinorhombic prisms, and in which M'' may be represented by magnesium, zinc, nickel, cobalt, iron, cadmium, or copper, and R' by sodium, potassium, or ammonium, but not by a metal of the other group.

There is no known sesquioxide of the alkaline metals, but there are some which are very important and characteristic in the groups of metals of which the atomic weights have been doubled by Cannizzaro. For instance, the sesquioxides of aluminium, iron, manganese, and chromium present important cases of isomorphism. The following oxides crystallise in the rhombohedral system:—

Al_2O_3	corundum,
Fe_2O_3	specular iron,
$(FeTi)O_3$	titaniferous iron (ilmenite),
Cr_2O_3	chromium oxide.

Analogous formulæ have been given to all these bodies, as well as to their isomorphous compounds, amongst which we may distinguish the spinels and the alums, which crystallise according to the regular system.

$MgO.Al_2O_3$	spinel,
$FeO.Fe_2O_3$	magnetic oxide of iron,
$MgO.Fe_2O_3$	pleonaste,
$ZnO.Al_2O_3$	gahnite,
$ZnO.Fe_2O_3$	franklinite.

The spinels form a very natural isomorphous group, and it is a well-known fact that their metallic elements often replace each other in the same crystal, without change of form. Thus, to take a single example, franklinite forms crystals in which Zn is replaced by Fe or Mn and Fe_2 by Mn_2.

It is unnecessary here to draw up a complete list of the alums $(SO_4)_3M_2.SO_4R_2+24H_2O$, in which M is aluminium, iron, manganese, or chromium, and R potassium, sodium, or ammonium.

The examples which we have just quoted show that the new system of atomic weights is in harmony with the law of isomorphism; isomorphous elements have received atomic weights which allow us to give analogous formulæ to the similar compounds in which these elements occur. In our exposition of the origin of this discovery we have already indicated the assistance which, in certain cases, may be derived from it in determining atomic weights, when for a given element considerations of a chemical order leave us to choose between several values.

There are, however, a few reservations which must be made in connection with the inferences to be drawn from isomorphism in the determination of atomic weights.

In the first place we must clearly comprehend the definition of isomorphism. All bodies presenting identical forms, even with a similar composition, are not necessarily isomorphous. In order to be so the elements said to be isomorphous must be able to replace each other in the same crystal, as, for example, is the case with red silver, SbS_3Ag_3 (pyrargyrite), and with proustite, AsS_3Ag_3, with the spinels, garnets, alums, &c. The following bodies, though they possess identical forms and a similar composition, are not isomorphous, as was formerly supposed :—

NO_3Na sodium nitrate,
CO_3Ca calcium carbonate (Iceland spar).

NO_3K potassium nitrate (saltpetre),
CO_3Ca calcium carbonate (arragonite).

This must not be forgotten: considering the immense number of chemical compounds and the limited number of physical forms which they can affect, it must often happen that dissimilar compounds may appear under the same form, without authorising us to consider them as isomorphous. This, for example, is the case with the two iodides of mercury Hg_2I_2 and HgI_2, which both crystallise according to the quadratic system, and the angles of which are sensibly the same, as Des Cloizeaux has recently shown. Must we conclude that they are really isomorphous? This seems inadmissible. This conclusion would only be legitimate if we were to find well-defined crystals in which the two iodides were mixed.

In the second place, it may happen that compounds possessing different atomic structures crystallise under the same form and are truly isomorphous. No one will deny the isomorphism of potassium chloride and ammonium chloride, and of ammonia alum and ordinary alum, though the ammonium group NH_4 presents a different atomic structure to that of potassium K.

Marignac, one of the most eminent and most competent chemists in these matters, regards as isomorphous the double fluorides of titanium, the double oxyfluorides of niobium, and the double oxyfluorides of tungsten. He has observed that the following double fluorides and oxyfluorides, which have potassium or copper as base, crystallise under sensibly identical forms:—[1]

Potassium salts	$K_2TiF_6.H_2O$;	$K_2NbF_5O.H_2O$;	$K_2WF_4O_2.H_2O$.
Copper salts .	$CuTiF_6.4H_2O$;	$CuNbF_5O.4H_2O$;	$CuWF_4O_2.4H_2O$.

This is also true for the double fluorides of zinc, which form the following series:—

Zinc fluosilicate	$ZnSiF_6.6H_2O$,
Zinc fluotitanate	$ZnTiF_6.6H_2O$,
Zinc fluostannate	$ZnSnF_6.6H_2O$,
Zinc fluoxyniobate	$ZnNbOF_5.6H_2O$,
Zinc fluoxymolybdate	$ZnMoO_2F_4.6H_2O$

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[1] *Comptes rendus*, vol. lxxxiv

The isomorphism of the fluosilicates, fluotitanates, and fluostannates is easily explained by the fact that these salts have a similar atomic composition; but before we can bring the isomorphism of the preceding fluorides with the oxyfluorides into agreement with the law of Mitscherlich we must admit, with Marignac, that oxygen and fluorine are isomorphous elements, and consequently can replace each other in combinations, atom for atom, without producing any change of form.

Thus we see that the law of isomorphism gives rise to some difficulties, and must be applied with judgment in the determination of atomic weights. It will only prove of real utility, from the point of view in question, when restricted to certain groups of analogous bodies, and when the conclusions to which it may lead are formed under rigorous restrictions. For example, we have mentioned above the compounds of niobium, and will now add further that Marignac has made a very judicious use of the law of isomorphism in fixing the atomic weight of niobium and tantalum. The double fluoride of niobium and potassium is isomorphous with the double fluoride of tantalum and potassium; tantalic acid, Ta_2O_5, and niobic acid, Nb_2O_5, should therefore receive analogous formulæ, and the atomic weight of tantalum be given as 180 if that of niobium is 94. Now, the latter atomic weight has been derived from the vapour density of niobium chloride, $NbCl_5$, which has been determined by H. Deville and Troost.

It is in such cases as these that the law of isomorphism affords valuable information, when its indications can be connected with the positive intelligence drawn from the law of volumes or the law of specific heats. In the determination of molecular and atomic weights the latter laws give more efficient aid to chemistry than the law of isomorphism, although the enunciation of these laws may not be strictly accurate from a physical point of view. We have already made this remark in connection with the law of specific heats which is an incomplete law (p. 125). The same remark applies, though in a less degree, to the law of volumes. In fact, the laws of Gay-Lussac and that of Avogadro and Ampère are dependent upon the law of Mariotte, and are in a manner forced to follow its variations.

CHAPTER VI.

THE NEW SYSTEM OF ATOMIC WEIGHTS RESPECTS AND RENDERS EVIDENT THE ANALOGIES WHICH EXIST BETWEEN BODIES.

DUMAS—MENDELEJEFF.

I.

The new system of atomic weights renders evident numerous analogies which have been discovered in chemistry, between either the elements themselves or between their compounds or reactions, thus dealing with the most varied and the most profound questions of science. It is a vast subject, which might be developed to a great length, but of which we shall here only endeavour to give a sketch.

Chemistry is not merely an immense collection of facts, but more exactly the science which teaches us to classify and arrange them, and this classification should begin with the elements themselves. Attempts have, we know, for some time been made in this direction.

The first, which was the most satisfactory, is due to Dumas. Admitting the distinction between the metals and the metalloids, Dumas proposed to divide the latter bodies into five families—namely, those of hydrogen, chlorine, sulphur, phosphorus, and boron. The principle, moreover, of this classification—that of comparing bodies which form similar compounds—agrees with the natural method. We shall not now dwell upon this point, which will be developed presently, but merely give Dumas' division of the metalloids into five families.[1]

1st family: hydrogen.
2nd family: fluorine, chlorine, bromine, iodine.
3rd family: selenium, sulphur. Appendix: oxygen.
4th family: phosphorus, arsenic. Appendix: nitrogen.
5th family: boron, silicon. Appendix: carbon.

Time has made little alteration in this attempt at classification. The bodies added as appendices have become the heads of their respective families. The only change that has been made has been to separate boron from carbon and silicon. Attempts have long been made to form the metals into similar groups. But here the problem becomes much more complicated, because, in the case of a great number of metals, the analogies are much less strongly marked, and the extreme terms of each group disagree to some extent in their properties and in the nature of their compounds. Thus certain metals constitute a transition between the several groups, and these intermediary terms only serve to put difficulties in the way of classification. Nevertheless, several groups of metals have been established. We will mention, in the first place, the alkaline metals, to which may be added, as an appendix, silver, thallium, and, to a certain point, copper and gold.

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[1] *Traité de Chimie appliquée aux Arts,* t. i., Introduction, p. lxxvii. We owe the term *metalloids* to Simon, who proposed it in 1808 to designate the metals of the alkalis and of the earths resembling the metals properly so called. In 1811 Berzelius applied the term to the non-metallic elements. (H. Kopp, *Geschichte der Chemie,* t. iii. p. 96.)

A second group comprises—

Calcium
Strontium
Barium,

to which may be added on the one hand—

Lead,

on the other—

Magnesium
Zinc
Cadmium.

Cobalt, nickel, iron, and manganese are connected with the preceding series through zinc. But this group throws some difficulties in the way of classification, as iron and manganese, which offer some analogies with the metals of the magnesium series, are connected, from another point of view, with both chromium and aluminium.

Another group of metals is connected with silicon, and comprises—

Titanium
Zirconium
Tin.

The following metals are connected with the family of nitrogen, phosphorus, and arsenic:—

Vanadium
Antimony
Bismuth
Niobium
Tantalum.

Molybdenum and tungsten present many mutual analogies, and resemble chromium and uranium.

Copper is difficult to classify. In the nature of its compounds it is not unlike mercury, but it also presents analogies with silver, and from this point of view resembles the alkaline metals.

Finally, the metals which accompany platinum have always been grouped into one family, which may be subdivided into three classes—i.e. ruthenium-osmium, rhodium-iridium, palladium-platinum.

The metals which form part of these families or classes are characterised by the analogy of the compounds which they form with the metalloids, particularly with oxygen and chlorine; for here, unfortunately, hydrogen compounds are wanting. Similar formulæ are accorded to a given group of the compounds in question, if appropriate atomic weights are assigned to the latter.

Each group of metals differs from the rest in the nature of its compounds. This is an established fact, and will be developed presently. But it was formerly unknown, having only recently been discovered, that the characteristic properties of the elements, which determine the nature of their compounds, are dependent upon the atomic weights.

Chemists such as Gladstone, Cooke, Pettenkofer, Odling, Kremers, and Dumas had pointed out certain numerical relations existing between the atomic weights of bodies belonging to a given group.

Thus, to quote a few examples from Dumas, very simple relations exist between the 'equivalents' of the bodies belonging to the families of oxygen, lithium, and magnesium. The numbers expressing these 'equivalents' form part of arithmetical progressions $a + xd$.

	Oxygen.	Sulphur.	Selenium.	Tellurium.
$a = 8$	8	16	40	64
$d = 8$	a	$a + d$	$a + 4d$	$a + 7d$

	Lithium.	Sodium.	Potassium.
$a = 7$	7	23	39
$d = 2 \times 8$	a	$a + d$	$a + 2d$

	Magnesium.	Calcium.	Strontium.	Barium.
$a = 12$	12	20	44	68
$d = 8$	a	$a + d$	$a + 4d$	$a + 7d$

We shall notice, as Pettenkofer has already done, that in these three families, the differences between the equivalents of the analogous elements are represented by 8 or by a multiple of 8.

In the families of fluorine and nitrogen we meet with the following relations, which are not quite so simple :—

	Fluorine.	Chlorine.	Bromine.	Iodine.
$a = 19$	19	35·5	80	127
$d = 16{\cdot}5$	a	$a + d$	$a + 2d + d$	$2a + 2d + 2d$
$d' = 28$				

	Nitrogen.	Phosphorus.	Arsenic.	Antimony.	Bismuth.
$a = 14$	14	31	75	119	207
$d = 17$	a	$a+d$	$a+d+d'$	$a+d+2d'$	$a+d+4d$
$d' = 44$					

The comparison of these numerical relations has led to an ingenious inference. If the homologous radicals of organic chemistry are formed by the addition of $n\mathrm{CH}_2$ to a given compound, why should we not suppose that the metals themselves are formed by the addition of a given species of matter, differing only in the manner of condensation? This was Prout's hypothesis, which reappears under another form, but even when thus transformed does not admit of a definite conclusion. Nevertheless we may derive from all these facts and considerations the following conclusion: the properties of bodies are dependent upon the atomic weights, and when we observe a great resemblance between a certain group of elementary bodies we shall also find a certain regularity in the increase of their atomic weights.

II.

The work of Mendelejeff has lately thrown a new light upon the relations existing between the atomic weights of elements and their properties. The latter are a function of the atomic weights, which function is *periodic*. Such is the proposition of the Russian chemist. It is not limited to such and such a group of elements, but embraces all the elementary bodies of chemistry. It is not limited to the consideration of certain analogies, but comprises all physical and chemical properties. It is simple in its principle and productive in its results. All the elements are arranged according to the increasing value of their atomic weights. We thus find that from one element to another the figures expressing these atomic weights only differ by a few units. We also remark that the properties are gradually modified as the atomic weights increase; that these modifications, moreover, do not advance continuously from the first term to the last, but pass through several cycles or periods. The differences between the atomic weights of contiguous elements are appreciably equal, but not absolutely so; and even in some cases we find very considerable discrepancies, as if there were a gap between contiguous elements. Mendelejeff has pointed out several, and it is a remarkable fact that one of these gaps has since been filled up. Lecoq de Boisbaudran's gallium had its place assigned in Mendelejeff's list. Its density had been accurately foreseen from the number, which was very near the truth, assigned to its atomic weight. The synthesis of the Russian chemist is thus a powerful one, and must in future be taken into consideration whenever we undertake a classification of bodies in accordance with their properties and reactions, or, in a word, regard the facts of chemistry from a lofty and comprehensive point of view.

The following example will explain Mendelejeff's conception :—

Let us take the fourteen elements whose atoms are the lightest after that of hydrogen, and arrange them in two horizontal lines, following the progression of their atomic weights.

Li = 7; G = 9·4; B = 11; C = 12; N = 14; O = 16; F = 19.
Na = 23 Mg = 24; Al = 27·3; Si = 28; P = 31; S = 32; Cl = 35·5.

In these two groups of simple bodies physical properties and chemical characters manifest gradual modifications proportional to the increase in the atomic weights. Thus the densities increase regularly, so that they reach a maximum about the middle of the series and afterwards diminish. Again, the atomic volumes—that is to say, the volumes which would be occupied by quantities proportional to the atomic weights, and which are the quotient of the atomic weights by the densities—naturally follow an inverse proportion to that of the densities; they decrease regularly, reaching a minimum about the middle of the series (see the table further on).

Thus, taking only the second group (the three last terms of the first are gaseous), we have, for the different simple bodies of which it is composed, the following densities and atomic volumes:—

	Na	Mg	Al	Si	P	S	Cl
Densities	0·97	1·75	2·67	2·49	1·84	2·06	1·38
Atomic vol.	24	14	10	11	16	16	27

We find, moreover, that the volatility diminishes from sodium to silicon, and increases again after silicon.

The chemical characters of the metals belonging to these groups are also subject to regular variations. Between each term differences are found in the fundamental chemical properties, which differences are manifested by the nature of the compounds. Among these compounds Mendelejeff has considered those formed with hydrogen or chlorine, and especially with oxygen. In these two groups the three first terms do not form combinations with hydrogen; such combinations do, however, occur in the last four, and here we may note the remarkable peculiarity that in these hydrogen compounds the number of hydrogen atoms decreases regularly from four to one (see the following table).

As we have just remarked, the metals which form the first terms of the two preceding groups do not enter into combination with hydrogen; they unite, on the other hand, with chlorine, and their capacity of combination with this element increases regularly. This double variation is shown in the following table:—

LiCl	GCl_2	BCl_3	CCl_4; CH_4	NH_3	OH_2	FH
NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$; SiH_4	PH_3	SH_2	ClH

A similar regularity may be observed in the oxygen compounds: the number of oxygen atoms, with which the metals forming the two groups can combine, increases regularly from the first to the last.[1]

Li_2O	G_2O_2*	B_2O_3	C_2O_4*	N_2O_5	—	—
Na_2O	Mg_2O_2*	Al_2O_3	Si_2O_4*	P_2O_5	S_2O_6*	Cl_2O_7

Another interesting peculiarity consists in the fact that the chemical functions of all these oxygen compounds are gradually and regularly modified from term to term, the first being strong bases, the intermediate ones indifferent bodies, and the last powerful acids.

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[1] The formulæ marked with an asterisk have been doubled, so as to make the regularity in question more striking.

Now, the chief characteristic of all these variations is the fact that they are repeated *in both groups,* so that the first term of one agrees with the first term of the other (Li with Na), the second with the second (G with Mg), and so on. Supposing all these elements to be arranged one after the other, we distinguish, as far as the variations of properties are concerned, *two periods,* the one beginning with lithium, the other with sodium. This is what Mendelejeff calls *the periodic law.* He extends it to all elementary bodies, and expresses it in the following terms: *the properties of elements* (and consequently those of the compounds which they may form) *stand in periodic relation to their atomic weights.*

In the following table all the simple bodies are arranged according to the progression of their atomic weights, and, in addition to this, are made to form horizontal and vertical series.

The horizontal series consist of elements resembling each other in their atomic weights, and of which the properties are gradually modified, so as to complete the period.

The vertical series consist of elements connected by the whole of their properties, and which may be termed homologous. The elements given in these vertical series form natural families.

H = 1	Li	G	B	C	N	O	F			
Atom. weights	7·02	9·3	11	12	14·04	15·96	19·1			
Densities .	0·59	2·1	2·68	3·3	—	—	—			
Atomic vol. .	11·9	4·4	4·1	3·6	—	—	—			
	Na	Mg	Al	Si	P	S	Cl			
Atom. weights	23	24	27·3	28	31	32	35·5			
Densities .	0·97	1·74	2·49	2·56	2·3	2·04	1·38			
Atomic vol. .	23·7	13·8	10·7	11·2	13·5	15·7	25·7			
	K	Ca	?	Ti	V	Cr	Mn	Fe	Co	Ni
Atom. weights	39·14	39·90	—	48	51·2	52·4	54·8	55·9	58·6	58·6
Densities .	0·86	1·57	—	—	5·5	6·8	8	7·8	8·5	8·8
Atomic vol. .	45·4	25·4	—	—	9·3	7·7	6·9	7·2	6·9	6·7
	Cu	Zn	Ga	?	As	Se	Br			
Atom. weights	63·3	64·9	69·9	72	74·9	78	79·75			
Densities .	8·8	7·15	5·96	—	5·67	4·6	2·97			
Atomic vol. .	7·2	9·1	11·7	—	13·2	16·9	26·9			
	Rb	Sr	Y	Zr	Nb	Mo	?	Ru	Rh	Pd
Atom. weights	85·2	87·2	89·6	90	94	95·8	—	103·5	104·2	106·2
Densities .	1·52	2·50	—	4·15	6·27	8·6	—	11·3	12·1	11·5
Atomic vol. .	56·1	34·9	—	21·7	15	11·1	—	9·2	8·6	9·2

	Ag	Cd	In	Sn	Sb	Te	I			
Atom. weights	108	111·6	113·4	117·8	122	128 ?	127			
Densities .	10·5	8·65	7·42	7·29	6·7	6·25	4·95			
Atomic vol. .	10·3	12·9	15·3	16·1	18·2	20·5	25·6			
	Cs	Ba	Ce	La	?	Di				
Atom. weights	132·15	136·8	137	139	—	147				
Densities .	—	3·75	—	—	—	—				
Atomic vol. .	—	36·5	—	—	—	—				
	?	?	Er	?	Ta	W	?	Os	Ir	Pt
Atom. weights	—	—	170·6	—	182	184	—	198·6	196·7	196·7
Densities .	—	—	—	—	10·8 ?	19·13	—	21·4	21·15	21·15
Atomic vol. .	—	—	—	—	16·9	9·6	—	9·3	9·3	9·3
	Au	Hg	Tl	Pb	Bi					
Atom. weights	196·2	200	203·6	206·4	210					
Densities .	19·3	13·59	11·86	11·83	9·82					
Atomic vol. .	10·2	14·7	17·1	18·1	21·1					
	?	?	?	Th		U				
Atom. weights	—	—	—	233·9		240 ?				
Densities .	—	—	—	7·7		18·3				
Atomic vol. .	—	—	—	30·4		13·1				

We have given this table at length, that the reader may estimate the true value of the attempt at classification in question, which, for the first time, embraces all the elements known to chemistry. This attempt, doubtless, still presents many imperfections, greatly due to the uncertain state of our present knowledge, especially with regard to rare elements. Thus tellurium is not in its place, supposing its atomic weight to have been accurately determined. If tellurium were the intermediate element between antimony and iodine it should possess an atomic weight of about 125. A question might also be raised as to whether copper is correctly placed : it is separated from certain elements—mercury, for example, which it appears to resemble. Other simple bodies, such as cobalt and nickel, the atomic weights of which are very similar, if not identical, also give rise to a difficulty. According to the principle of the classification, their properties should similarly coincide, which is not the case. And yet we know that these metals have many points in common. This is also the case with chromium, manganese, and iron, which are placed side by side in the same horizontal series, and between the atomic weights of which there is very little difference. On the other hand, great differences may be observed between the properties of vanadium and bromine, between potassium and calcium, between rubidium and ruthenium, which yet are so closely related by their atomic weights. In the same manner we must confess that the variations or gradations of properties are far from progressing regularly or uniformly in the different groups. In some cases they are too great, as in the first group, carbon, nitrogen, oxygen, and fluorine; in others too slight, as we have just remarked, for the last terms of the third group. Though it may be generally true that the properties of bodies are subject to periodic modifications with the increase of their atomic weights, the law of these modifications escapes our observation, and seems to be of a complicated nature; for, on the one hand, the atomic weights of successive elements vary within considerable limits, without displaying any regularity in these variations; on the other hand, we must confess that the gradations of properties, or, in other words, the greater or less divergencies between the properties of successive elements, do not appear to depend upon the degree of the differences between the atomic weights. These are real difficulties.

In the preceding table we are principally struck, at first sight, with the gaps which may be noticed between two elements, the atomic weights of which show a greater difference than two or three units, thus marking an interruption in the progression of the atomic weights. Between zinc (64·9) and arsenic (74·9) there were two, one of which has been recently filled up by the discovery of gallium. We must, however, remark that the considerations by which Lecoq de Boisbaudran was led in the 'search' for gallium (for this great discovery is not due to chance) have nothing in common with the conception of Mendelejeff. Again, though gallium has filled up a gap between zinc and arsenic, and though other gaps may be subsequently filled, it is by no means proved that the atomic weights of the new elements will be those assigned to them by the principle of classification which we have been discussing.

In fact, the atomic weight of gallium is sensibly different to that which was predicted by Mendelejeff. It is also possible that the future may be reserving for us the discovery of a new element, the atomic weight of which will closely resemble or coincide with that of a known element, as the atomic weight of nickel coincides with that of cobalt, and as that of potassium closely resembles that of calcium, and such a discovery would not fill any foreseen gap. For example, if cobalt were unknown, it would not be discovered by Mendelejeff's principle of classification. This imperfection is undoubtedly due to the fact mentioned above, that the rate of increase in the atomic weight of elements belonging to the same period (horizontal series) is altogether irregular.

III.

Among the physical properties dependent upon atomic weight we have not yet mentioned density. Other physical properties seem in the same manner to be subject to periodic variations with the increasing value of the atomic weights. We may mention particularly malleability, fusibility, volatility, and conductibility for heat and electricity. Without entering into the details of this subject, we may give an outline of all the facts, drawing our information from a graphic construction for which we are indebted to Lothar Meyer, who has contributed a detailed and important development to Mendelejeff 's idea. (See the end of the volume.)

The elements are arranged upon the axis of the abscissæ, at distances from zero proportional to their atomic weights, each element occupying a fixed point upon the axis. At this point an ordinate is drawn, which represents the atomic volume of the given element. The curve which joins the extremities of the ordinates represents, therefore, the variations of the atomic volumes. From the absence or uncertainty of the data relative to certain gaseous or other little studied elements, it has been impossible to give the entire curve. In particular an important gap is visible between didymium and tantalum, and in other places dotted lines are used, where certain unknown atomic volumes are interpolated.[1] This being granted, the graphic construction shows at once that the variations of the atomic volumes (and consequently of the densities) are periodic. Starting from lithium, the curve sinks till it reaches a minimum which corresponds with boron; it then rises, attaining a second maximum with sodium. At this point it descends again, then rises to a third maximum with potassium, and so on. Now it is proved that the position occupied by the elements upon this curve is in relation with their physical and chemical properties.

In the first place, as far as the densities are concerned, it is evident, from the very principle upon which the curve is constructed, that the light metals (possessing considerable atomic volumes) should occupy the maxima, and the heavy metals (possessing low atomic volumes) the minima; but the fact which particularly demands our attention is that, with atomic volumes sensibly identical, two metals may possess very different properties, as they are situated upon the ascending or descending portion of the curve.

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[1] The atomic volumes of elements may be indirectly determined by deducing them from the molecular volumes of their liquid or solid compounds (see Chapter VII.)

The ductility, fusibility, and volatility of elements are related to their atomic weights, and are subject to periodic variations with the increase of their atomic weight. The light metals, which occupy the summits, or the immediately succeeding descending portion of the curve, are ductile. The heavy metals, occupying the minima, or the ascending portion near the minima, of the curve, are partially ductile in the fourth, fifth, and sixth groups.[1] Take, for example, the fourth, which comprises the elements placed, from the progression of their atomic weights, between potassium and rubidium. The light metals, potassium and rubidium, which stand at the top of the curve, are ductile. A decrease should be observed in the ductility of the elements placed upon the descending branch, till at the bottom we meet with brittle metals, such as vanadium, chromium, and manganese. From iron, which follows, the ductility increases with the elements which occupy the minima, or the immediately succeeding ascending branch. Ductile copper is the last of this ascending series. With gallium the ductility again decreases; arsenic is brittle.

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[1] The three first groups only contain heavy metals.

Thus we see that in the fourth group of elements, while the density increases and diminishes regularly with the increase of the atomic weight, from potassium to rubidium, the ductility diminishes and increases twice. Thus the variations of ductility extend to two groups instead of one, as is the case with density. It also appears that elements which have evidently the same atomic volume, such as chromium and copper, vanadium and zinc, differ to a striking extent in ductility. Vanadium and chromium, situated upon the descending branch of the curve, are brittle; copper and zinc are ductile, though in a different degree. And since we have drawn attention to the elements ranged in group IV between potassium and rubidium, we may remark that there was a considerable gap between zinc ($Zn = 64{\cdot}9$) and arsenic ($As = 74{\cdot}9$). It was here that Mendelejeff placed his 'ekaluminium,' which is the gallium of Lecoq de Broisbaudran.

From the place of this element, between zinc and arsenic, though nearer to zinc, Mendelejeff was able to predict that its density would be about 5·9. Now Lecoq de Boisbaudran has found it to be 5·96. From the place occupied by gallium in the third vertical series on p. 159 the eminent Russian chemist was able to discover a connection with aluminium, which is found to be correct; thus gallium oxide resembles aluminium oxide.

We should be exceeding the limits which we have imposed upon ourselves in this treatise, if we gave fresh developments and examples of the relations which exist between the atomic weights and other physical properties. It must suffice to say that fusibility and ductility are, with the progression of atomic weights, subject to variations similar to those manifested by ductility and density. Crystalline form and expansibility by heat appear also to be dependent upon the atomic weights. Fizeau's careful researches upon the coefficients of expansion of a certain number of simple bodies [1] is well known. The results obtained by the eminent physicist show that this coefficient increases and diminishes regularly, as the atomic weight rises. Here, again, we observe the periodicity in the variations of properties, which is the striking characteristic of Mendelejeff's law.[2]

The relations which exist between atomic weights and specific heats were discovered by Dulong and Petit. We gave them on p. 124, observing that the atomic heats are not precisely identical, but that the law of Dulong and Petit is subject to irregularities, and that the latter are in a certain measure due to the degree of impurity, to the want of homogeneity in the solid bodies, and to the variations to which the specific heats are subject in a given body, according to the temperature. But Lothar Meyer has remarked that the elements which only approximately obey the law of Dulong are generally those of which the atomic weights as well as the atomic volumes are low. This is the case with carbon, boron, and silicon.

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[1] *Comptes rendus*, vol. lxviii. p. 1125.

[2] L. Meyer has illustrated the influence of the atomic weigh's upon the expansion by heat in a table similar to that upon p. 159, but in which the vertical series are so disposed that the three last terms of the third group, Fe, Co, Ni, become the first of the fourth. For these developments we refer our readers to the excellent work of Lothar Meyer. The same chemist has pointed out and discussed the relations which exist between the atomic weights and the coefficient of refrangibility, the conductibility for heat and electricity. (*Die modernen Theorien der Chemie*, Breslau, 1877.)

Amongst the elements with low atomic weights which nevertheless obey the law of Dulong, must be placed, lithium, sodium, magnesium, and potassium, which, on the other hand, possess a high atomic volume—that is to say, their density is low. We are, therefore, led to conclude that the irregularities to which the law of Dulong and Petit is subject are not only due to the causes which we have enumerated above, but are also related to the different volumes occupied by the ultimate particles of bodies—that is to say, to the atomic volumes. Atoms which occupy the smallest volumes have a lower specific heat—in other words, require a little less heat in undergoing the same variations of temperature than the more 'voluminous' atoms of other elements.

Be this as it may, Dulong and Petit were the first to show that the specific heats of simple bodies are dependent upon the atomic weights, for they decrease regularly as the latter increase. And here, it must be observed, the variation is not periodic.

We must point out one more relation which exists between the atomic weights and a physical property of bodies—the power, namely, of emitting luminous rays. In fact, Lecoq de Boisbaudran has proved that for analogous elements, such as potassium, rubidium, and cæsium—calcium, strontium, and barium—aluminium, gallium, and indium, the increase of atomic weight is proportional to the increase of wave-length, which corresponds with the spectral lines of each of these metals. This profound idea was developed by the eminent chemist before the Chemical Society of Paris, but has not yet received sufficient publicity. We can only give the statement, observing that it has received a most striking confirmation from the discovery of gallium, and that it was possible to calculate very exactly the atomic weight of this metal, with those of aluminium and indium, from the position of the 'corresponding' spectral lines of these three metals.

Such are some of the relations which exist between the atomic weights and the physical properties of simple bodies. It is an important chapter, to which Mendelejeff and Lothar Meyer have contributed many valuable developments; and amongst the theoretical consequences which follow from the conception of the Russian chemist we may mention the following: it contributes new elements to the classification of simple bodies, and controls views founded upon other considerations. A few remarks upon this subject will be necessary.

IV.

In the table upon pp. 159, 160 the elements are arranged in groups and series. The vertical columns are composed of elements which resemble each other in the whole of their properties, and especially in the nature of their compounds. The elements are there arranged in families. If, with the increase of atomic weights, the properties of elementary bodies are subject to periodic variations, then those elements constituting a period may be placed in one *group*, and since in each of these groups the properties are subject to analogous variations, the corresponding terms of each group may also be connected: a certain concordance or harmony will be observed in these '*harmonic*' or '*homologous*' terms, which will form a *series*. In some of these series, if not in all, we shall find in the increase of the atomic weights that regularity which was pointed out at the commencement of this chapter. The result of the periodic law which considers the variations of properties in each group has therefore for a corollary a principle of classification or *seriation* which establishes analogies of properties in each family of analogous bodies. This is an important fact, and it is a circumstance worthy of remark that such varied and unexpected developments arise from the simple idea of arranging bodies according to the increasing value of their atomic weights. This simple idea was a most important one.[1]

The horizontal groups contain, as we have seen, groups of elements in which the *physical* properties are subject to periodic variations. We must now proceed to show how their *chemical* properties are gradually modified from term to term.

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[1] It is right to observe that Mendelejeff's idea is somewhat analogous to an idea long ago promulgated by De Chancourtois.

In the first place this is the case with the 'electro-chemical' character of elements. The variations to which the electro-chemical properties are subject from one term to another, and which were given for the first and second groups upon p. 156, appear also in the other groups, except that in some of these groups the variations from the first term to the last pass through two periods instead of one. This, for example, is the case with the group which commences with potassium and for that which commences with rubidium. Thus after potassium we have the electro-positive metal calcium, after which the electro-negative character appears in titanium, vanadium, and chromium. With manganese and iron the electro-positive character is again seen, becoming more pronounced with nickel and cobalt. This is also the case with the group which commences with electro-positive rubidium, and is closed by palladium, also electro-positive.

On the other hand, the group which commences with silver, an electro-positive metal, finishes with tellurium and iodine, both electro-negative.

The electro-chemical character of elementary bodies exercises some influence upon their power of combination with different elements. It is worthy of remark that those metals which are strongly electro-positive have great tendency to form with electro-negative oxygen the simple and generally stable compounds of the protoxides. The higher degrees of oxidation are rare and unstable. The contrary is the case with the electro-negative metals and metalloids; here the degrees of oxidation are numerous, and the higher terms, very rich in oxygen, form powerful acids.

Again, the nature of the compounds formed by the elements with electro-positive hydrogen increases in simplicity as the electro-negative character of the element becomes more pronounced. Hydrochloric, hydrobromic, and hydriodic acids may be quoted as examples.

As a general rule, in considering the power of combination with a given element possessed by the simple bodies which form part of one group, we observe a regular gradation, to which Mendelejeff has called attention. Without repeating the facts mentioned on p. 157, we may here remark that the capacity of combination with oxygen possessed by simple bodies increases regularly with their atomic weight to a certain point, after which it begins to decrease again. That such is the case will be seen from the following table, which contains some oxygen compounds of the different elements. Observe that the vertical series here correspond with the horizontal series of the table given on pp. 159, 160. It is also important to remark that, with a few exceptions, comprising the peroxides, the oxygen compounds quoted here are the richest known: they therefore show the limit of the capacity of combination with oxygen possessed by the elements.

Series of Oxygen Compounds.

(Li_2O)	Na_2O	K_2O	Cu_2O	Rb_2O	Ag_2O	Cs_2O	—	Au_2O
G_2O_2	Mg_2O_2	Ca_2O_2	Zn_2O_2	Sr_2O_2	Cd_2O_2	Ba_2O_2	—	Hg_2O_2
B_2O_3	Al_2O_3	—	Ga_2O_3	Y_2O_3	In_2O_3	Ce_2O_3	Er_2O_3	Te_2O_3
C_2O_4	Si_2O_4	Ti_2O_4	—	Zr_2O_4	Sn_2O_4	La_2O_3	—	Pb_2O_4
N_2O_5	P_2O_5	V_2O_5	As_2O_5	Nb_2O_5	Sb_2O_5	—	Ta_2O_5	Bi_2O_5
—	S_2O_6	Cr_2O_6	(Se_2O_6)	Mo_2O_6	Te_2O_6	Di_2O_3	W_2O_6	—
—	(Cl_2O_7)	Mn_2O_7	(Br_2O_7)	—	(I_2O_7)	—	—	—
—	—	(FeO_3)	RuO_4	—	OsO_4	—	—	—
—	—	Co_2O_3	RhO_2	—	IrO_2	—	—	—
—	—	Ni_2O_7	PdO_2	—	PtO_2	—	—	—

To make the progression in the power of combination of elements with oxygen clear, the formulæ of the oxides have been doubled in the second, fourth, and sixth horizontal series. This progression is at once seen upon glancing at the vertical series; but we also find that it attains a maximum at about the seventh or eighth term, after which we notice a diminution in the richness of oxygen. It appears, therefore, that the capacity of combination with oxygen possessed by simple bodies forming part of a given group passes through variations similar to those noticed above (p. 157) in connection with the compounds formed by the simple bodies of the first and second groups with oxygen, chlorine, and hydrogen. The periodic law is here again evident, as with the physical properties.

We must, in conclusion, notice one more peculiarity referred to by Mendelejeff.

The composition of the hydrates is naturally connected with that of the oxides. If, as is allowable, we regard the hydrates of the well-marked oxides as combinations of simple bodies with OH (hydroxyl) groups, we observe that two hydroxyl groups correspond to each atom of oxygen in an oxide, thus—

$$Ca''O + H_2O = Ca''(OH)_2.$$

This notation is now in general use; but Mendelejeff, who was one of the first to use it, remarks that the number of hydroxyl groups which a simple body has the power of fixing appears to be determined by the number of hydrogen atoms contained in its hydrogen compound, or again by the number of ethyl groups contained in the ethyl compound. Thus, to take an example from the sodium group, the electro-negative elements of this series follow each other in the following order: silicon, phosphorus, sulphur, chlorine. Now, we find that their most stable hydrates contain as many hydroxyl groups as their hydrides contain atoms of hydrogen and their ethides ethyl groups.

Hydrates.	Hydrides.	Ethylides.
$Si(OH)_4$	SiH_4	$SiEt_4$
$PO(OH)_3$	PH_3	PEt_3
$SO_2(OH)_2$	SH_2	SEt_2
$ClO_3(OH)$	ClH	$ClEt$.

These developments are sufficient, and we must conclude. It clearly results from the above that the most important physical properties and the fundamental chemical properties of simple bodies stand in some relation to their atomic weights: they are a function of the atomic weights. This is the result of general investigation, and, in spite of the uncertainty which still reigns as to the precise manner of this function, and notwithstanding some objections or imperfections of detail, we may say that the principle indicated by the Russian chemist will henceforth furnish one of the bases of chemical classification. Now, it is evident, in conclusion, that the relations in question would not appear, and the principle which connects them could not have been formulated without the adoption of the present system of atomic weights. These relations would have remained hidden or obscure had the attempt been made to deduce them from 'equivalents' I lay stress upon this point of view, and remark, finally, that the discoveries of the eminent Russian chemist furnish a strong argument in favour of the new system of atomic weights. Mendelejeff himself speaks very decidedly upon this point. These are his own words:—'Our conceptions upon atomic weights have latterly acquired such solidity, especially since we have applied to them the law of Avogadro and Ampère, and since the works of Laurent, Gerhardt, Regnault, Rose, and Cannizzaro, that we may confidently affirm that the idea of atomic weights—that is to say, the smallest quantity of an element contained in a molecule of its combinations—will continue without alteration through all the variations to which chemical theories may be subject.'[1]

V.

We must now consider the new system of atomic weights as furnishing new elements in the classification of simple bodies. The principle of this classification will be that of the natural method: each group must be composed of bodies which resemble each other in their chemical properties, in the nature, form, and functions of their principal compounds. Simple bodies belonging to the same family or series form similar compounds, and the atomic weights attributed to these simple bodies should be such that the similar compounds may receive analogous formulæ. This side of the question has already been touched upon in the preceding chapter, but it will be useful to return to it and to bring forward a few more proofs, drawn from purely chemical considerations, in favour of the system of atomic weights now generally adopted.

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[1] *Die periodische Gesetzmässigkeit der chemischen Elemente*, von D. Mendelejeff, p. 4; St. Petersburg, August 1871.

Arsenic and antimony are two closely related elements; their similar compounds should therefore receive analogous formulæ. Gerhardt was right in halving the atomic weight which had previously been attributed to antimony, the chlorides, oxides, and sulphides of these two simple bodies thus receiving the formulæ—

$AsCl_3$	$SbCl_3$
As_2O_3	Sb_2O_3
As_2O_5	Sb_2O_5
As_2S_3	Sb_2S_3,

which notation demonstrates the analogy of these compounds.

There is no difference of opinion upon this point, which, however, cannot be said for the double atomic weights which Cannizzaro has attributed to certain metals in order to make them agree with the law of Dulong and Petit, and also with the law of gaseous densities.

We remarked above that Berzelius had represented all protoxides by RO, while Gerhardt attributed to them all the formula R_2O. It is now admitted that there are two classes of protoxides. The first, R_2O, are formed of two atoms of metal and one of oxygen; the second contain a single atom of metal and one of oxygen. Now, is such a distinction founded upon a chemical basis, and are we authorised in separating the alkaline metals, to which may be added silver and thallium, which all form protoxides, R_2O, from the metals of the alkaline earths and so many others forming protoxides?

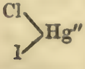
This classification is proved to be quite legitimate from the special character of the alkaline metals, which form a number of isomorphous and characteristic compounds.

Silver has been correctly classified with the alkaline metals. We may remind our readers of the isomorphism of anhydrous sodium sulphate and silver sulphate. We would also draw attention to the fact that in the alums and the double sulphates of the magnesian series, $SO_4R'' + SO_4M_2' + 6H_2O$, potassium may be replaced by sodium and ammonium, but not by calcium or barium.

Cream of tartar or acid potassium tartrate is easily saturated by sodium carbonate or by ammonia, and the mixed salts which are thus obtained—double potassium and sodium tartrate, and double potassium and ammonium tartrate—are as definite and stable as the neutral salt of potassium. If, on the contrary, cream of tartar is saturated with chalk, the result is a very unstable compound, which bears no resemblance to the sodio-potassium tartrate and others of that class.

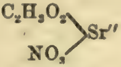
The following is a peculiarity of the same kind and equally characteristic. The alkaline metals, or rather the alkaline bases, have a marked tendency to form acid salts with the dibasic acids. The acid sulphates, carbonates, oxalates, and tartrates of potassium are very well defined, and relatively stable salts. The acid salts formed by the alkaline earths are, on the contrary, but few in number, and when we do meet with them they are very unstable and are decomposed by water. Thus there is no acid oxalate of calcium, and the acid oxalate of barium, which has been described, is so unstable that it cannot be dissolved in water.

It appears from these facts that the alkaline metals and the monovalent metals in general form a perfectly distinct group, and we shall find that the bivalent metals are equally well characterised by certain properties. Two atoms of chlorine or two residues of monobasic acids are required to saturate them. They can fix at the same time two different monatomic elements or two residues of different acids, and their capacity of combination accounts for the existence of compounds analogous to the following :—



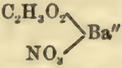
$\left.\begin{matrix}\mathrm{Cl}\\ \mathrm{I}\end{matrix}\right\rangle \mathrm{Hg}''$

Mercury chloro-iodide.



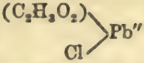
$\left.\begin{matrix}\mathrm{C_2H_3O_2}\\ \mathrm{NO_3}\end{matrix}\right\rangle \mathrm{Sr}''$

Strontium aceto-nitrate.



$\left.\begin{matrix}\mathrm{C_2H_3O_2}\\ \mathrm{NO_3}\end{matrix}\right\rangle \mathrm{Ba}''$

Barium aceto-nitrate.



$\left.\begin{matrix}\mathrm{(C_2H_3O_2)}\\ \mathrm{Cl}\end{matrix}\right\rangle \mathrm{Pb}''$

Plumbic aceto-chlorhydrin.

The argument derived from the existence of these mixed compounds in favour of the existence of bivalent metals, and, consequently, of the duplication of the atomic weights of these metals, is of the same order as that which was formerly drawn by Liebig from the constitution of the sodio-potassium tartrate in favour of the dibasicity of tartaric acid.

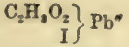
This group of bivalent metals is further distinguished by the tendency which is shown by their oxides to form dibasic salts. This, as is well known, is especially the case with the oxides of copper and lead.

The duplication of the atomic weights of calcium, magnesium, and lead enables us to represent in a very simple and striking manner the constitution of certain minerals belonging to the wagnerite and apatite group (see p. 139).

Take, for example, the latter mineral. It is generally represented as formed of 3 molecules of ordinary phosphate of lime and one molecule of calcium fluoride. This formula agrees with analysis, but it would be extremely difficult to demonstrate, on the dualistic theory of salts, the existence of such an unusual combination. If, however, we regard calcium as a bivalent metal, capable of replacing two atoms of hydrogen in phosphoric acid, we shall see that the presence of an atom of fluorine or chlorine is *necessary* to saturate the remaining affinities. Three molecules of ortho-phosphoric acid, PO_4H_3, contain 9 atoms of hydrogen. If we add 4 atoms of calcium, 8 atoms of hydrogen only are displaced and the acid is not saturated. If we add 5 atoms of calcium, the presence of which is attested by analysis, there will be an excess of calcium, for the fifth atom of this metal, only finding one atom of hydrogen to displace, will not be saturated: the atom of fluorine comes in to complete the saturation. The following formulæ will explain the combination from this point of view:—

$(PO_4)_3H_9$	$(PO_4)_3\left\{\begin{matrix}Ca_4{}''\\ H\end{matrix}\right.$	$(PO_4)_3\left\{\begin{matrix}Ca_4\\ (Ca''F)'\end{matrix}\right.$
3 molecules of phosphoric acid.	Calcium phosphate non-saturated.	Apatite.

In a great number of other compounds chlorine plays the part taken by fluorine in wagnerite and apatite. This is the case in the combinations described by Carius under the name of plumbic aceto-chlorhydrin, aceto-bromhydrin, and aceto-iodhydrin (p. 179).



$$\left.\begin{matrix}C_2H_3O_2\\ I\end{matrix}\right\}Pb''$$

Plumbic aceto-iodhydrin.

I have drawn attention to one more argument in favour of the duplication of atomic weights, and consequently of the bivalency of certain metals. In Gerhardt's notation the formulæ of a large number of hydrated salts had been so arranged that each molecule of the anhydrous salt contained a half-molecule or an uneven number of half-molecules of water. This inconvenience is removed if the atomic weights of the metals contained in these salts are doubled. I have given upon p. 463 of vol. i. of the 'Dictionnaire de Chimie pure et appliquée' a number of examples in explanation of the argument in question; but I must confess that for two reasons I now attribute less importance to this argument.

In the first place there are exceptions, for we find salts containing bivalent metals, a molecule of which crystallises with a half-molecule or an uneven number of half-molecules of water, so that if we wished to represent the water of crystallisation by entire molecules, we should have to take two molecules of the anhydrous salt.

In the second place, we must not forget that the smallest quantity of a crystal is a different matter to the smallest quantity of a salt—that is to say, a molecule—and we may well imagine that in the formation of a crystal 2 molecules of a salt may unite with 1 molecule or with an uneven number of molecules of water. We shall, however, presently discuss the water of crystallisation.

It appears from the above discussion, that chemical analogies, in agreement with the law of specific heats, the law of gaseous densities, and the law of isomorphism, authorise us in doubling the atomic weights of a great number of metals. The compounds of these metals receive, therefore, special formulæ, similar to those which were formerly given to them by Berzelius, and differing from those which we now attribute to the corresponding compounds of the alkaline metals. In fact, the compounds of the metals, whose atomic weights have been doubled, and which we call bivalent, may be placed, as regards their molecular complication, between the corresponding compounds of the alkaline metals and silver, and those formed by the sesquioxides.

For example:—

Oxides.	Hydrates.	Chlorides.	Nitrates.	Sulphates.
K_2O	$K(OH)$	KCl	NO_3K	SO_4K_2
Ag_2O		$AgCl$	NO_3Ag	SO_4Ag_2
$Ca\ O$	$Ca''(OH)_2$	$Ca''Cl_2$	$(NO_3)_2Ca''$	SO_4Ca''
$Pb\ O$	$Pb''(OH)_2$	$Pb''Cl_2$	$(NO_3)Pb''$	SO_4Pb''
$Sb_2'''O_3$	$Sb'''(OH)_3$	$Sb'''Cl_3$		$(SO_4)_3Sb_2'''$
$Bi_2'''O_3$	$Bi'''(OH)_3$	$Bi'''Cl_3$	$(NO_3)_3Bi'''$	$(SO_4)_3Bi_2'''$

The formulæ of the sesquioxides and the corresponding compounds are universally admitted, but some chemists refuse to adopt the notation which expresses the diatomic nature of certain metals. It complicates, they say, the demonstration of the science. Certain formulæ would undoubtedly gain in simplicity if we adopted for the metals in question the halved atomic weights; but are we justified in misrepresenting reactions and ignoring the most evident analogies under the pretext of simplicity? The universal acceptance of the notation in question, as regards organic compounds, shows emphatically how natural and correct it is as regards mineral compounds. This point deserves explanation.

We represent the action of hydriodic acid upon the hydrates of potassium and lead by the following equations :—

$$\begin{aligned} &K(OH) + HI = KI + H_2O \\ &Pb''(OH)_2 + 2HI = PbI_2 + 2H_2O. \end{aligned}$$

It would be simpler, they say, to halve the second by halving the atomic weight of lead,[1] and to write—

$$\mathit{Pb}'(OH) + HI = \mathit{Pb}'I + H_2O.$$

The latter would unquestionably be simpler, and strictly equivalent to the former. But it is an important fact that the formula $Pb''(OH)_2$ and the equation in which it is given enable us to trace an interesting connection and demonstrate an evident analogy—that, namely, which exists between the hydrates of mineral chemistry and those of organic chemistry. These hydrates of potassium and lead correspond to the hydrates of ethyl and ethylene, and the action of hydriodic acid upon the latter hydrates is represented by the following equations :—

$$\underset{\substack{\text{Ethyl hydrate} \\ \text{(alcohol).}}}{C_2H_5(OH)} + HI = \underset{\substack{\text{Ethyl} \\ \text{iodide.}}}{C_2H_5I} + H_2O$$

$$\underset{\substack{\text{Ethylene dihydrate} \\ \text{(glycol).}}}{C_2H_4''(OH)_2} + 2HI = \underset{\substack{\text{Ethylene} \\ \text{iodide.}}}{C_2H_4I_2} + 2H_2O$$

Who would now think of halving the latter under the pretext of rendering it more simple and exactly comparable to the first equation?

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[1] $Pb = 206{\cdot}4$; $\mathit{Pb}' = 103{\cdot}2$.

Berthelot himself, who upheld this antiquated argument, could not consent to write—

$$\underset{\text{Ethylene hydrate.}}{CH_2(OH)} + HI = \underset{\text{Ethylene iodide.}}{CH_4I} + H_2O$$

It is generally admitted by chemists that the ethylene compounds should, to a certain extent, rank between the ethyl compounds and the glycerine compounds, and that the series to which they belong increase in complication, as may be seen from the mineral compounds given in the preceding table. We have a curious connection and an evident parallelism between the mineral and organic oxides, hydrates, chlorides, and salts.

Oxides.	Hydrates.	Chlorides.	Acetates.
$(C_2H_5')_2O$ Ethyl oxide.	$C_2H_5'.OH$ Ethyl hydrate.	$C_2H_5'.Cl$ Ethyl chloride.	$C_2H_5'.C_2H_3O_2$ Ethyl acetate.
$(C_2H_4'')O$ Ethylene oxide.	$C_2H_4''(OH)_2$ Ethylene hydrate. (glycol).	$C_2H_4''.Cl_2$ Ethylene chloride.	$C_2H_4''(C_2H_3O_2)_2$ Ethylene acetate
	$C_3H_5'''(OH)_3$ Glyceryl hydrate (glycerine).	$C_3H_5'''.Cl_3$ Glyceryl chloride (trichlorhydrin).	$C_3H_5'''(C_2H_3O_2)_3$ Glyceryl acetate (triacetin).
	$C_4H_6^{\text{iv}}(OH)_4$ Erythrite.	$C_4H_6^{\text{iv}}.Cl_4$ Erythryl chloride.	$C_4H_6^{\text{iv}}(C_2H_3O_2)_4$ Erythryl acetate.

It is also worthy of remark that the reactions which produce these compounds or by which they are transformed also show a regular gradation and increasing complication. Take, for example, the action of potash upon the mineral salts and upon the ethers we have just mentioned. It brings into play one, two, or three molecules of alkali, and produces mineral and organic hydrates, which are exactly comparable to each other, as regards the degree of hydration. Thus, potash reacts in the following manner upon the metallic nitrates :—

$NO_3Ag + KOH = NO_3K + AgOH$[1]
$(NO_3)_2Pb'' + 2KOH = 2NO_3K + Pb''(OH)_2$
$(NO_3)_3Bi''' + 3KOH = 3NO_3K + Bi'''(OH)_3$.

The second reaction naturally takes its place between the first and the third reactions.

In organic chemistry we meet with a similar gradation. When potash reacts upon the ethers, one, two, or three molecules of alkali take part in the reaction, as in the preceding case, according to the more or less complex nature of the ether :—

$$\underset{\text{Ethyl acetate.}}{C_2H_3O_2.C_2H_5'} + KOH = \underset{\text{Potassium acetate.}}{C_2H_3O_2.K} + \underset{\text{Alcohol.}}{C_2H_5'(OH)}$$

$$\underset{\text{Ethylene acetate.}}{(C_2H_3O_2)_2C_2H_4''} + 2KOH = \underset{\text{Potassium acetate.}}{2(C_2H_3O_2.K)} + \underset{\substack{\text{Ethylene dihydrate} \\ \text{(glycol).}}}{C_2H_4''(OH)_2}$$

$$\underset{\substack{\text{Glyceryl triacetate} \\ \text{(triacetin).}}}{(C_2H_3O_2)_3(C_3H_5''')} + 3KOH = \underset{\text{Potassium acetate.}}{3(C_2H_3O_2.K)} + \underset{\substack{\text{Glyceryl trihydrate} \\ \text{(glycerine).}}}{C_3H_5'''(OH)_3}$$

In these mineral and organic hydrates we see that the number of the groups (OH) which marks their degree of hydration increases regularly, just as the atoms of chlorine increase in the corresponding chlorides. Again, the chlorides and hydrates of the second class are necessarily and naturally intermediary between the first and third class. It is, therefore, an incontestable fact that these compounds, and the reactions which give rise

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[1] Since silver hydrate does not exist, the equation must be written—

$$2NO_3Ag + 2KOH = 2NO_3K + Ag_2O + H_2O.$$

to or modify them, differ in their form. Chemistry would be a very simple science if this form were the same for all compounds, and if all reactions were, to some extent, cast in the same mould. The system of atomic weights, which is now generally adopted, shows that there is a regular gradation in these forms of combination and in these reactions, and brings to light the harmony which exists between the reactions of mineral chemistry and those of organic chemistry. It is the last argument which we add to all those which we have already advanced in favour of this system of atomic weights.

CHAPTER VII.

ATOMIC AND MOLECULAR VOLUMES.

By the term atomic volumes of simple bodies is meant the volumes occupied by quantities of these bodies proportional to their atomic weights, and by the term molecular volumes of compound bodies, the volumes occupied by quantities of these bodies proportional to their molecular weights.

To determine the relative volumes occupied by atoms, we have only to divide the atomic weights by the weights of the unit of volume—that is to say, by the densities. The atomic volumes are the quotients of the atomic weights by the densities; the molecular volumes, the quotients of the molecular weights by the densities.

If matter were continuous, these quotients would give the true volumes occupied by atoms relatively to the volume of one of them taken as unity. But this is not the case.

The ultimate particles of bodies do not touch each other; they are separated by relatively large spaces. They move in ether, and in gaseous bodies their distance apart is immense in proportion to their size: it is very considerable in solid and liquid bodies. The space occupied by the unit of volume of bodies is therefore far from being filled by the atomic substance itself; it comprises a portion of ether probably considerable. In other words, the conception of the density of bodies comprises two distinct but inseparable elements—namely, the ultimate particles which we term atoms or molecules, and the interatomic or intermolecular spaces. This remark will show the exact meaning which must be attached to the expressions 'atomic volumes' and 'molecular volumes.'

If the molecules were situated at equal distances in the different bodies, it is clear that a given volume of the latter would contain the same number of molecules; the molecular weights would be proportional to the densities and the molecular volumes uniform. This is the case with the gases. We admit that they do perceptibly contain, in a given volume, the same number of molecules; the relative weights of the latter are proportional to the densities. But it is different with solid and liquid bodies. Their molecules are situated at various distances, not only in different substances, but sometimes in the same body. Thus their coefficients of expansion are very different, and, moreover, vary for a given body, according to the temperature and physical condition of that body. This unequal distribution of molecules in solid and liquid bodies makes it impossible to discover a simple relation between the molecular weights and the density, like that which we have just mentioned in connection with gaseous bodies.

As regards liquid and solid elements, we know that very wide limits must be assigned to the variations of their densities.

The lightest of metals, lithium, has a density of 0·59 and weighs 39 times less than the same volume of hammer-hardened platinum, the density of which is 23. These densities, moreover, vary according to the physical condition of the body, so that it is impossible to compare the densities of liquid and solid bodies, of amorphous and crystallised bodies, of bodies solidified after fusion and bodies beaten and hammer-hardened after solidification. In order to draw any comparisons from the atomic volumes of simple bodies and the molecular volumes of compound bodies, we must, therefore, calculate the densities under similar conditions—namely, for liquid bodies, at equal distances from their points of ebullition, as Hermann Kopp recommends; and for solid bodies, as much as possible at equal distances from their points of fusion.

We will now proceed to give a brief account of the result of this work and of all the facts which have been collected with regard to the relative volumes occupied by atoms and molecules. We shall confine ourselves to general results, referring our readers to special works for numerical data and details.

The limits within which the atomic volumes of simple bodies vary are less considerable than in the case of densities, though still very wide. Mendelejeff has shown that these variations are a periodic function of their atomic weights; for if the elements are arranged in the order of the progression of their atomic weights, their atomic volumes increase and decrease periodically.

We have discussed this point at some length, and will not, therefore, return to it. We will only add that the numerical values of the atomic volumes of simple bodies will be found in the table given upon pp. 159, 160.

It appears from these facts that there must be a relation between atomic weights and atomic volumes. Of the precise nature of this relation we are, however, ignorant.

Dumas has remarked that certain simple bodies belonging to the same family have almost the same atomic volumes. This is the case with the following bodies:—

Atomic Volumes	Atomic Volumes	Atomic Volumes
Chlorine 25·6	Sulphur 15·7	Phosphorus 13·5
Bromine 26·9	Selenium 16·9	Arsenic 13·2
Iodine 25·6	——	——
	Tellurium 20·5	Antimony 18·2
		Bismuth 21·1

We see that tellurium, antimony, and bismuth only partially conform to this rule; the following elements break through it entirely:—

Atomic Volumes	Atomic Volumes	Atomic Volumes
Carbon 3·6	Lithium 11·9	Calcium 25·4
Silicon 11·2	Sodium 27·3	Strontium 34·9
Zirconium 21·7	Potassium 45·4	Barium 36·5
	Rubidium 56·1	

We owe all our accurate information upon the molecular volumes of compound bodies to the extensive researches of Hermann Kopp, who devoted his attention principally to the molecular volumes of liquid bodies. The results of these researches may be summed up in the following propositions, which apply especially to organic liquids.

1. The molecular volume of compounds is expressed by the sum of the atomic volumes occupied by the elements.

2. In compounds possessing a similar atomic composition, the same element always possesses the same atomic volume. The latter being determined for every simple body, it follows that the molecular volume of a compound may be calculated if the atomic composition is known.

3. In compounds possessing different atomic structures the same element may occupy two different volumes. Thus, to borrow an expression from the theory of types, the atomic volume of oxygen differs with its position either as contained in a radical, or situated without that radical, in the state of typical oxygen. Nitrogen possesses a different atomic volume, according as it is contained in a compound derived from the ammonia type, combined with carbon as in cyanogen, or united to oxygen as in nitrous vapour.

Hermann Kopp succeeded in determining the atomic volumes of carbon, hydrogen, oxygen, nitrogen, &c., by means of ingenious considerations which we shall briefly describe as follows.

1. In comparing the molecular volumes of organic compounds, which differed from each other only by $n\text{CH}_2$, he found that for each addition of CH_2 the average increase of the volume of the molecule was 22.

We may therefore conclude that this number expresses the volume of one atom of carbon and two of hydrogen —that is to say, the volume of CH_2.

2. Two organic compounds which differ from each other by the addition of nC and the loss of nH_2 possess the same molecular volume. We may, therefore, conclude that C occupies the same volume in these compounds as H_2, and as the molecular volume of CH_2 is 22, it follows that the atomic volume of carbon is 11 and that of H is $\frac{11}{2} = 5{\cdot}5$.

3. The molecular volume of water at boiling point is 18·8 (instead of 18). If we subtract 11, the volume of H_2, we have 7·8 for the atomic volume of oxygen. According to Hermann Kopp, oxygen only occupies this volume in organic compounds when it is contained in a typical residue, to use the expressions of that time—that is to say, when it is connected with two different atoms which it unites, as, for instance, the two atoms of hydrogen in water. It occupies a different volume when it is contained in a radical—that is to say, combined by its two points of saturation to the same atom of carbon as in aldehyde and acetone.[1]

Aldehyde containing C_2H_4O—that is to say, $2CH_2 + O$ —the volume which is here occupied by oxygen may be found by subtracting from the molecular volume of aldehyde (56 to 56·9) that of $2CH_2 = 44$. We thus obtain 12 to 12·9 as the atomic volume of oxygen when contained in an organic radical.

Hermann Kopp adopts the mean 12·2.

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[1] The two forms of oxygen compounds are given in the following table, which will explain the distinction in question :—

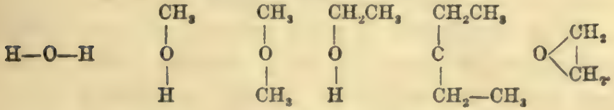
Having thus calculated, by means of the above considerations, the volumes occupied in organic compounds by the atoms of carbon, hydrogen, and oxygen, the eminent chemist was able to calculate *à priori* the molecular volumes of a number of ternary organic compounds, by adding together the sum of the atomic volumes of the elements, in accordance with one of the propositions given above. The molecular volume of a compound containing *a* atoms of carbon, *b* atoms of hydrogen, *c* atoms of oxygen in the radical, and *d* atoms of typical oxygen, may therefore be given by the formula—

COMPOUNDS CONTAINING TYPICAL OXYGEN.

Typical Formulæ.

Water.	Methyl hydrate.	Methyl oxide.	Ethyl hydrate.	Ethyl oxide.	Ethylene oxide.
$\left.\begin{matrix}H\\H\end{matrix}\right\}O$	$\left.\begin{matrix}CH_3\\H\end{matrix}\right\}O$	$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}O$	$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$	$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$	C_2H_4O

Constitutional Formulæ.

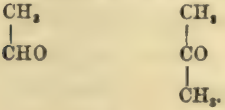


COMPOUNDS CONTAINING OXYGEN IN THE RADICAL.

Typical Formulæ.

Aldehyde.	Acetone.
$\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}$	$\left.\begin{matrix}C_2H_3O\\CH_3\end{matrix}\right\}$

Constitutional Formulæ.



$$\begin{matrix}CH_3\\|\\CHO\end{matrix}\qquad\qquad\begin{matrix}CH_3\\|\\CO\\|\\CH_3.\end{matrix}$$

$$MV = a11 + b5{\cdot}5 + c12{\cdot}2 + d7{\cdot}8.$$

The molecular volumes calculated in this manner have been compared with those deduced from experiment, when the molecular weights are divided by the densities taken at boiling point. The agreement between calculated and experimental results in a great number of cases is sufficient to justify a serious consideration of Hermann Kopp's conclusions.

Omitting the consideration of the facts relative to the atomic volumes of other elements, such as sulphur, nitrogen, chlorine, bromine, and iodine, indirectly deduced from the molecular volumes of liquid compounds containing these elements, by means of processes similar to those just discussed, we must add a few words upon the molecular volumes of solid bodies. We must here confine ourselves to a few results regarding certain bodies endowed with a similar constitution and obtained under the same physical conditions.

It is found that a great number of isomorphous bodies have the same molecular volume. This is the case with the sulphates of the magnesian series $SO_4M'' + 7H_2O$, with the double sulphates of the magnesian series $SO_4M'' + SO_4R_2 + 6H_2O$, and with the alums. It seems, however, impossible to calculate the molecular volumes of solid compounds by means of the atomic volumes from the principles laid down for liquid bodies. Here the data of the problem are different. In proof of this we may, in conclusion, refer our readers to the relations pointed out by Playfair and Joule between the molecular volumes of certain crystallised salts and that of the water which they contain. We should suppose that the molecular volume of the crystallised salt would be equal to the sum of the volumes of the anhydrous salt and the water. But it is not so. In certain salts rich in water of crystallisation, such as the arsenates and phosphates which contain 12 molecules, and in the crystals of carbonate of soda which contain 10, the volume of this water (taken as solid) is equal to the volume of the molecule of the crystallised salt, the molecules of the anhydrous salts being as it were interposed between the molecules of water, without augmenting the volume of the latter.

BOOK II.

ATOMICITY;

OR VALENCY OF ATOMS IN COMBINATION.

CHAPTER I.

DEFINITION AND HISTORIC DEVELOPMENT OF THE IDEA OF ATOMICITY.

In the preceding pages we have traced the origin and foundation of the atomic theory. We have seen this simple and correct idea which was brought forward by Dalton—namely, that the invariable proportions in which bodies combine represent the relative weights of their ultimate particles—gradually gain ground in science. We have explained the principles upon which the determination of these weights rests, as well as the physical laws by means of which these determinations are guided and controlled, thus rendering to the hypothesis of atoms, which belongs to the department of chemistry, assistance all the more unexpected and efficacious as coming from a different department of science. In concluding our explanation of the present system of atomic weights, we met with the idea that the ultimate particles of bodies, which we call atoms, do not all possess the same combining value: we saw that, while one atom of potassium unites with one atom of chlorine to form a chloride, an atom of lead takes two atoms of chlorine, and an atom of antimony three or even five. This difference in the power possessed by simple bodies of forming more or less complex combinations with another simple body must be considered as a peculiar property, inherent in their ultimate particles, and in order to distinguish it from affinity, which implies the *force* of combination, it has been termed *atomicity*, which is synonymous with combining *value* or *valency of atoms*. We must now show how this idea was first introduced into science, the precise sense in which it must be accepted, and the consequences resulting from it which affect chemical theories.

These are fresh facts which give rise to fresh ideas. And the facts which are connected with the idea in question may be given as follows in their historical order, the unequal saturating capacity possessed by bases for acids, and the unequal saturating capacity possessed by acids for bases.

The first group of facts were long unknown. Berzelius refused to admit the existence of sesquioxides, capable of saturating 3 molecules of acid, when protoxides could only saturate one. Gay-Lussac attributed to these sesquioxides a constitution strictly equivalent to that of the protoxides, so that one molecule of oxide (an equivalent) should saturate one molecule (an equivalent) of acid. Some time afterwards, when the existence of polyacid bases was admitted, though set aside with other facts whose theoretical signification was not considered, Graham discovered polybasic acids. This discovery created a sensation and caused some difficulty in the conception and definition of equivalent quantities (see p. 76). Nevertheless fifteen years passed before the significance of this fact was recognised from the point of view now occupying our attention.

In the memorable work which was published in 1851 upon etherification, and which marks a new era in the history of chemical doctrines, Williamson, generalising an idea first published by Laurent and Sterry Hunt, brought forward the proposition that a great number of organic and mineral compounds may be referred to the type of water. He held that such was the case with monobasic acids and with the salts derived from them. Acetic acid, for example, and potassium acetate were represented by the formulæ—

$$\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O \qquad \left.\begin{matrix}C_2H_3O\\K\end{matrix}\right\}O,$$

which are constructed upon the model of that of water—

$$\left.\begin{matrix}H\\H\end{matrix}\right\}O,$$

the radical C_2H_3O and potassium, K, taking the place of an atom of hydrogen. But the eminent English chemist also perceived that polybasic acids, which are not equivalent to the monobasic, present a greater molecular complication, and should be referred to a condensed water type. Thus dibasic sulphuric acid was regarded as being derived from 2 molecules of water,

$$\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2,$$

by the substitution of the radical SO_2 for two atoms of hydrogen. The formula of sulphuric acid becomes therefore,

$$\left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2$$

and the radical SO_2 here takes the place of two atoms of hydrogen. Williamson has written this in two lines, and how productive of developments has this idea been which was announced with such simplicity. Odling, by an ingenious notation which is still in use, first marked this difference in the capacity for saturation possessed by the acetyl and sulphuryl radicals, by giving to their formulæ a different index—

$\left.\begin{matrix}(C_2H_3O)'\\H\end{matrix}\right\}O$	$\left.\begin{matrix}(SO_2)''\\H_2\end{matrix}\right\}O_2$
Acetic acid.	Sulphuric acid.

The idea that the substituting value of sulphuryl is twice that of acetyl is clearly expressed in this notation. We here find the germ of the modern theory of radicals which underwent such important developments a few years later, and which has superseded the old conceptions of Lavoisier, Berzelius, and Liebig. This theory is still accepted, as well as the notation by which it is perpetuated and represented,[1] though it is now subordinate to a more general theory of which it appears as the natural consequence. We must now trace this further development.

In the first place we should notice that, on the occasion of his fine researches upon the organo-metallic compounds, Frankland called attention, in 1872, to the power which metals possess of combining with a fixed and definite number of atoms. This idea, which was then new, formed the starting point of the theory of the saturation of elements and contains the germ of the theory of atomicity.

In a note upon the theory of glycerine compounds[2] the author showed that glycerine may be regarded as a hydrate of the radical C_3H_5 and its composition represented by the formula $\left.\begin{matrix}(C_3H_5)'''\\ H_3\end{matrix}\right\}O_3$, which is similar to the formulæ by which, in accordance with the ideas of Williamson, ordinary phosphoric acid, $\left.\begin{matrix}(PO)'''\\ H_3\end{matrix}\right\}O_3$, is represented. In fact, the several series of glyceric ethers are comparable to the several series of ordinary phosphates or orthophosphates.[3] This radical, $(C_3H_5)'''$, which can replace 3 atoms of hydrogen, is formed by the subtraction of 3 atoms of hydrogen from the saturated hydrocarbon C_3H_8. Starting from this fact, which was then acknowledged as true, and has not since been invalidated by any fresh facts, that those hydrocarbons which are richest in hydrogen belong to the series C_nH_{2n+2}, among which we find the hydrocarbon C_3H_8 (propane), the author has derived the radical C_3H_5 from that hydrocarbon by the subtraction of 3 atoms of hydrogen. He proves that the radical C_3H_7, which can replace one atom of hydrogen, comes from the same hydrocarbon by the loss of a single atom of hydrogen. The subtraction of an atom of hydrogen developes a force in this residue C_3H_7, in virtue of which it is impelled to combine again with this hydrogen atom of which it has been deprived, or with some equivalent to it, and, on the other hand, this same force makes it ready to supply the place of an atom of hydrogen wherever it is wanting. Again, the loss of three atoms of hydrogen creates in the residue $C_3H_5 = C_3H_8 - H_3$ a force by which it is ready to replace three atoms of hydrogen. Glycerine is produced in this manner, by the substitution of such a radical for three atoms of hydrogen in the type of three condensed molecules of water.

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[1] The formulæ $C_2H_3O.OH$ and $SO_2(OH)_2$, now in general use, are only a variation of those used by Williamson.

[2] *Ann. de Chimie et de Phys.*, 8$^{\mathrm{e}}$ sér. t. xliii. p. 492.

[3] And not, as was stated by Berthelot in his remarkable memoir, to the phosphates, pyrophosphates, and metaphosphates.

$$\left.\begin{matrix} H_3 \\ H_3 \end{matrix}\right\} O_3 \qquad\qquad \underset{\text{Glycerine.}}{\left.\begin{matrix} (C_3H_5)''' \\ H_3 \end{matrix}\right\} O_3}$$

The author has even gone further. He supposed that the five atoms of hydrogen were divided in the following manner among the three atoms of carbon [$C_3H_5 = CH_2-CH-CH_2$], which to my knowledge is the first attempt that was made at such a distribution of atoms in a radical. It resulted, however, in nothing, being a simple supposition. It was some years afterwards that Kekulé showed the ruling principle by which such distributions of atoms may be conducted in a rational manner.

There was a gap between the 'monobasic' radical $(C_3H_7)'$ and the 'tribasic' radical $(C_3H_5)'''$, which the author was discussing. The residue C_3H_6 obtained by the subtraction of two atoms of hydrogen from the hydrocarbon C_3H_8, should possess a substituting or combining value equivalent to these two atoms of hydrogen. This proved to be the case from the study of Dutch liquid and its analogues, which resulted in the discovery of the glycols. This residue or radical C_3H_6 is propylene, and can replace, like its homologue ethylene, two atoms of hydrogen in two condensed molecules of water. The bodies possessing this constitution are the glycols.

$$\left.\begin{array}{r} H_2 \\ H_2 \end{array}\right\} O_2 \qquad \underset{\text{Glycol.}}{\left.\begin{array}{r} (C_2H_4)'' \\ H_2 \end{array}\right\} O_2} \qquad \underset{\text{Propyl glycol.}}{\left.\begin{array}{r} (C_3H_6)'' \\ H_2 \end{array}\right\} O_2}$$

These 'diatomic' radicals, as from that time they have been called, can also combine directly with two atoms of chlorine or bromine, as the Dutch chemists showed at the end of the last century. The author has remarked that the phenomena belong to the same class as those presented by the direct combination of a metal with chlorine or bromine.

Thus the substituting value marks the combining value. There is a connection between the two, and ethylene, which can replace 2 atoms of hydrogen, can combine directly with 2 atoms of chlorine or bromine, or, again, with 2 atoms of hydrogen (Berthelot) or their equivalent. In the same manner the radical sulphuryl $(SO_2)''$, which can replace 2 atoms of hydrogen in 2 condensed molecules of water (p. 199), can also combine with 2 atoms of chlorine to form sulphuryl chloride $(SO_2)''Cl_2$ (Regnault). The radicals of mineral and organic chemistry possess, therefore, as far as their combining or substituting value is concerned, all the attributes of simple bodies. This substituting value of radicals, correlative with the combining capacity, has received a definite name: it was then, and is still, called 'atomicity.' We shall soon extend it to the elements themselves (p. 211), of which the radicals, as just defined, are but in a measure the representatives.

I believe it is to Odling that the credit is due of having been the first clearly to enunciate the idea that the substituting or combining value of simple bodies is not the same. He attributed to ferric hydrate the formula $\left.\begin{matrix}Fe'''\\H_3\end{matrix}\right\}O_3$, caustic potash being represented by the formula $\left.\begin{matrix}K'\\H\end{matrix}\right\}O$. In the hydrate of sesquioxide of iron the metal therefore replaces 3 atoms of hydrogen, while potassium in caustic potash only replaces one atom of hydrogen.

$\left.\begin{matrix}H\\H\end{matrix}\right\}O$ Water.	$\left.\begin{matrix}K'\\H\end{matrix}\right\}O$ Potash.
$\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_3$ 3 molecules of water.	$\left.\begin{matrix}Fe'''\\H_3\end{matrix}\right\}O_3$ Ferric hydrate.

In his memoir upon radicals[1] the author has given a similar formula to phosphorous acid, which he represented as $\left.\begin{matrix}P'''\\H_3\end{matrix}\right\}O_3$.

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[1] *Ann. de Chim. et de Phys.* (3), t. xlvi. p. 307. The author even proposed the hypothesis that the phosphorus in some manner en-

Nitrogen has been represented as a tribasic element derived from the type of three condensed molecules of hydrogen.

$$\underset{\text{Hydrogen.}}{\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}}\qquad\underset{\text{Ammonia.}}{\left.\begin{matrix}H_3\\N'''\end{matrix}\right\}}\qquad\underset{\text{Nitrogen.}}{\left.\begin{matrix}N'''\\N'''\end{matrix}\right\}}$$

Oxygen and sulphur, the 'dibasic' character of which was demonstrated by Kekulé, were regarded as derived from a condensed type of 2 molecules of hydrogen.

$$\underset{\text{Hydrogen.}}{\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}}\qquad\underset{\text{Water.}}{\left.\begin{matrix}H_2\\O''\end{matrix}\right\}}\qquad\underset{\text{Free oxygen.}}{\left.\begin{matrix}O''\\O''\end{matrix}\right\}}$$

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croached upon the 3 molecules of water, as if an atom of phosphorus, P, were formed of 3 sub-atoms $p_3 = P$, each of which would replace an atom of hydrogen in a molecule of water, the residues of the 3 molecules of water, each of which would have lost an atom of hydrogen, being thus saturated by the *tribasic* phosphorus.

$$\underset{\text{3 molecules of water.}}{\begin{matrix}\left.\begin{matrix}H\\H\end{matrix}\right\}O\\\left.\begin{matrix}H\\H\end{matrix}\right\}O\\\left.\begin{matrix}H\\H\end{matrix}\right\}O\end{matrix}}\qquad\qquad\underset{\text{Phosphorous acid.}}{\begin{matrix}\left.\begin{matrix}p\\H\end{matrix}\right\}O\\\left.\begin{matrix}p\\H\end{matrix}\right\}O\\\left.\begin{matrix}p\\H\end{matrix}\right\}O\end{matrix}}$$

The idea that the atom of triatomic phosphorus is formed by the union of 3 sub-atoms, has been variously developed. It was abandoned by the author because he found that in pentachloride of phosphorus and phosphoric acid the atom of phosphorus must be divided into 5 sub-atoms. The idea of types served as a basis for this idea, but we see at once how much it contributed towards showing that elements have different substituting and combining values, and consequently that their atoms are not mutually equivalent.

Chlorine, on the contrary, and the elements of that class, were, after Gerhardt, referred to the hydrogen type.

$$\begin{array}{ccc}\left.\begin{matrix}H\\H\end{matrix}\right\} & \left.\begin{matrix}H\\Cl'\end{matrix}\right\} & \left.\begin{matrix}Cl'\\Cl'\end{matrix}\right\} \\ \text{Hydrogen.} & \text{Hydrochloric acid.} & \text{Free chlorine.}\end{array}$$

Thus the elements which we have just mentioned were regarded as differing from each other in their substituting value, phosphorus and nitrogen replacing or combining with 3 atoms of hydrogen; oxygen and sulphur replacing or combining with 2 atoms of hydrogen; while chlorine could only unite with, or replace, a single atom.

II.

The idea that hydrochloric acid was derived from 2 volumes of hydrogen by the substitution of 1 volume of chlorine for 1 volume of hydrogen, or, again, that it was derived from 2 volumes of chlorine by the substitution of 1 volume of hydrogen for 1 volume of chlorine, was fundamentally a very old one. Dumas had remarked as early as 1828 that in the combination of 1 volume of chlorine with 1 volume of hydrogen, a combination which produces 2 volumes of hydrochloric acid, the atoms of hydrogen and the atoms of chlorine seemed to be halved.[1] The idea was perfectly correct, though stated in words which made it erroneous. If Dumas had taken 2 volumes of hydrogen and chlorine instead of 1 volume, and spoken of molecules instead of atoms divided into half-atoms, he would have given to his proposition a definite form, which may be clearly expressed by the following formulæ :—

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[1] *Traité de Chimie appliquée aux Arts,* t. i., Introduction, p. xxxviii. Berzelius in his treatise energetically protests against this idea of Dumas, which would have led the great French chemist,

$$\begin{array}{ccccccc} \left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\} & + & \left.\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix}\right\} & = & \left.\begin{matrix}\mathrm{H}\\ \mathrm{Cl}\end{matrix}\right\} & + & \left.\begin{matrix}\mathrm{H}\\ \mathrm{Cl}\end{matrix}\right\} \\ \text{2 vol.} & & \text{2 vol.} & & \text{2 vol.} & & \text{2 vol.} \\ \text{(1 molecule)} & & \text{(1 molecule)} & & \text{(1 molecule)} & & \text{(1 molecule)} \\ \text{of hydrogen.} & & \text{of chlorine.} & & \multicolumn{3}{c}{\text{of hydrochloric acid.}} \end{array}$$

Under any circumstances it is evident that the important distinction which we find in Dumas's conception between two species of ultimate particles, atoms and half-atoms (which we now call molecules and atoms), appears again in science long after the ideas of Avogadro and Ampère had sunk into oblivion. Free hydrogen

had it been adopted and developed, to a truer conception of the theory of volumes than that which satisfied the learned Swede. This conception of Dumas is, I think, so important, that the passage in which he states it should be given in his own words.

'These considerations are so simple that it is needless to dwell longer upon them. With the application, however, comes the difficulty. Take a litre of chlorine, and let us suppose it to contain 1,000 atoms; a litre of hydrochloric acid should contain the same number. Now,

1 litre of hydrogen = 1,000 atoms
and 1 litre of chlorine = 1,000 atoms
forming 2 litres of hydrochloric acid = 2,000 atoms.

But each atom of chlorine upon combining with one atom of hydrogen can only produce one atom of hydrochloric acid, or 1,000 atoms in all. We must, then, admit that the atoms of chlorine and hydrogen are halved in order to form the atoms of hydrochloric acid. Each of the latter are therefore composed of a half-atom of hydrogen and a half-atom of chlorine. This is also the case with deutoxide of nitrogen.'

and chlorine are formed of two atoms *combined with each other*. The latter feature is important, and was added by Gerhardt, who expressed the same thought in these words: free chlorine is a chloride of chlorine, free hydrogen a hydride of hydrogen. Such was the new idea which was to make its way into science. To represent the molecules of diatomic gases as composed of two atoms *combined* with each other, was to admit that these atoms have a mutual affinity, similar to that which unites the dissimilar atoms of compounds; to regard the hydrogen molecule as belonging to the same class of combination as hydrochloric acid; to represent the direct combination of chlorine with hydrogen as a double decomposition; and to restore, in a word, though in a simpler form, the proposition of Avogadro and Ampère and the beautiful conception of Dumas.

Thus hydrogen, chlorine, oxygen, and nitrogen are formed, in a free state, of 2 atoms combined with each other. This proposition is supported by a number of chemical proofs.

It is well known that even finely divided copper is scarcely attacked by hydrochloric acid at ordinary temperatures. Hydride of copper, on the contrary, is attacked by it with great energy. Brodie was the first to observe that this reaction was easily explained if, in addition to the affinity of chlorine for copper, the affinity of hydrogen for hydrogen was admitted.

$$[1]\mathrm{Cu}\overset{-}{\mathrm{H}} + \overset{+}{\mathrm{H}}\mathrm{Cl} = \mathrm{CuCl} + \overset{-}{\mathrm{H}}\overset{+}{\mathrm{H}}.$$

As regards oxygen, the conception in question has received startling confirmation from the celebrated experiments of Brodie upon the reciprocal action of peroxides. The fact that peroxide of hydrogen reduces oxide of silver, permanganic acid, and perchromic acid so easily, and at the same time is itself reduced with a brisk liberation of oxygen, was formerly explained as the action of contact, an expression which means nothing. Brodie ascribed it to the natural play of affinities. The oxygen which is added to water in hydrogen peroxide unites with the oxygen of the oxide of silver or with the excess of oxygen in the highly oxidised acids, and one atom of oxygen uniting with another forms a molecule of oxygen which contains both atoms and is evolved. This affinity of oxygen for oxygen is stronger than that of water for oxygen and than that of peroxide of manganese for oxygen. This is why bodies saturated with oxygen can reduce each other, without a combination taking place between the products of this reduction.

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[1] Cu = 63.

Another class of arguments may be brought forward in support of this important idea. The peculiar activity of hydrogen and oxygen *when in the nascent state* is undoubtedly due to the fact that under these circumstances the atoms act separately, before they have been united to another atom to form the pairs of which the molecules are composed. It is evident that heat should be disengaged by this formation, which is a combination. The isolated atoms which are just formed and not yet united into pairs are still provided with this heat, and have, consequently, the greater activity.[1]

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[1] This idea was published long ago by P. A. Favre (*Comptes Rendus*, t. lxiii. p. 369)

Berthelot has uselessly brought forward in opposition to this conception considerations drawn from the thermal phenomena which accompany the formation of the unstable combinations just mentioned Hydride of copper, he said, was undoubtedly formed with absorption of heat: it is not astonishing therefore that it should be attacked in the cold by hydrochloric acid, when copper is not. The argument seems to rest upon giving a natural explanation of the reaction in question. But some reserves must be made upon the premises. What meaning must be attached to the proposition, hydride of copper is formed with absorption of heat? No chemical combination can give rise, as a combination, to an absorption of heat, for the connection and fixation of the ultimate particles of bodies in new positions of equilibrium gives rise to a loss of energy, and consequently to a disengagement of heat. It is, however, possible for this action to be preceded or accompanied by an inverse action—that is to say, by a separation of the ultimate particles, a phenomenon which gives rise to an absorption of heat. These two actions, upon superposition, give rise to a result sometimes positive, sometimes negative, according to their respective intensity. We cannot say, therefore, that copper and hydrogen have absorbed in the act of combining a certain quantity of heat: they have, on the contrary, liberated heat. But, while separating from the combination which contained them in the first place,[1] the elements of the hydride of copper might have absorbed more heat: the thermal result is therefore unquestionably negative.

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[1] This combination is hypophosphorous acid, the action of which upon sulphate of copper gives rise to the formation of copper hydride.

As regards the reciprocal reductions of peroxides, Berthelot again observes that hydrogen peroxide, ozone, and probably oxide of silver, as well as the metallic acids mentioned above, are formed with absorption of heat. The fact is here unimportant and the argument no longer to the point. For though their instability would be rendered intelligible from the admission that these metallic acids and peroxide of hydrogen contain more heat than the lower oxides to which they are reduced, this fact would not explain their *reciprocal* reduction.

Free nitrogen has a weak affinity for the greater number of the other elements, and can only combine indirectly with a great number, often with absorption of heat. The reason is very simple: the heat liberated by the combination of nitrogen with chlorine is less than the heat which is absorbed when the diatomic molecules of nitrogen and chlorine are resolved into two atoms. If, therefore, heat is disengaged by the decomposition of nitrogen chloride, it simply proves that more heat is liberated on the reconstitution of these molecules containing two similar atoms than is absorbed on the separation of the atoms in nitrogen chloride. This all argues in favour of the modern idea that the molecules of certain simple bodies are formed of several atoms which exercise a certain mutual attraction, or expend upon each other, entirely or in part, the affinities with which they are endowed.

III.

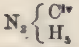
Kekulé has made an important advance in this direction. This eminent chemist, from a consideration of its simplest combinations, was the first to recognise the fact that carbon should be regarded as quadrivalent. For, in its saturated compounds, a single atom of carbon is united with 4 atoms of hydrogen in marsh gas, with 4 atoms of chlorine in carbon chloride, with 3 atoms of hydrogen and 1 atom of chlorine in methyl chloride, and with 3 atoms of chlorine and 1 atom of hydrogen in chloroform. Again, it is united with 2 atoms of oxygen, which are equal to 4 of hydrogen, in carbonic acid gas, and in carbon disulphide with 2 atoms of sulphur, which are equal to 4 of hydrogen. This is sufficient, for though the list of compounds in question is far from being complete, the demonstration is so well known that further remark is unnecessary. Carbon is therefore a quadrivalent, or, in the language of that time, a tetratomic element, which means that its capacity of combination with hydrogen is four, while that of nitrogen is three, oxygen two, and chlorine one. The following table will show the increasing capacity of combination of these four elements:—

$Cl'H$ hydrochloric acid,
$O''H_2$ water,
$N'''H_3$ ammonia,
$C^{iv}H_4$ marsh gas.

Moreover, their capacity of combination is equal to their substituting value, for, if 1 atom of carbon in combining with hydrogen is saturated with 4 atoms of this gas, it will be also able to replace 4 atoms of this gas. Thus guanidine, for example, may be regarded as derived from 3 molecules of ammonia by the substitution of 1 atom of carbon for 4 atoms of hydrogen

N_3H_9

3 molecules of ammonia.



$$N_3\left\{\begin{array}{l}C^{iv}\\H_5\end{array}\right.$$

Guanidine.

This is also the case with the atoms of nitrogen, oxygen, and chlorine, which can respectively replace 3 atoms, 2 atoms, or 1 atom of hydrogen, as in the following compounds :—

$(C_6H_5)H_3NCl$ — Aniline chlorhydrate.

$(C_6H_5)N'''NCl$ — Diazobenzene chloride.

$C_2H_5.OH$ — Alcohol.

$C_2H_3O''.OH$ — Acetic acid.

$C_2H_3O.OH$ — Acetic acid.

$C_2H_2Cl'O.OH$ — Monochloracetic acid.

Thus the capacity of combination of *elements* determines their substituting value. These two ideas are correlative, and are expressed by the term 'atomicity.'

Atomicity is therefore identical with the *valency* of atoms, and it seems necessary to introduce this term into scientific language, for it is clear, and it cannot be replaced by that of equivalence, because this value or valency is different for different atoms. There are univalent, bivalent, trivalent, and quadrivalent atoms. The elements are also termed monatomic, diatomic, triatomic, and tetratomic, though there is one objection to this nomenclature, for the same terms are used with a different meaning to designate the gases or vapours of simple bodies the molecules of which are formed of 1, 2, or 4 atoms. This confusion should be avoided.

In the series of hydrogen compounds enumerated above, the valency of the atoms is indicated by the number of hydrogen atoms with which they are severally united. The atoms of chlorine are so constituted that they can only fix one atom of hydrogen, while the oxygen atoms can fix two, the nitrogen atoms three, and the carbon atoms four, to form saturated hydrogen compounds. The capacity of saturation of the carbon atoms is therefore four times greater than that of chlorine for the same element, the unit of saturation being represented by 1 atom of hydrogen. And if 1 atom of carbon were united with only 3, or 2 atoms, of hydrogen, one unit of saturation would be wanting in the first case and two in the second.

But this is not all. Kekulé has gone further, and has shown that the carbon atoms can unite with each other, and thus satisfy some of the affinities which are inherent to them. This fact is so important that we think right to reproduce here the proof of the eminent chemist. It is founded upon the fact that in saturated hydrocarbons the number of hydrogen atoms never exceeds the limit indicated by the formula C_nH_{2n+2}. The following are examples:—

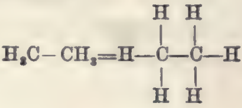
Hydrocarbons	C_nH_{2n+2}
Methane	CH_4
Ethane	C_2H_6
Propane	C_3H^8
Butane	C_4H_{10}
Pentane	C_5H_{12}
Hexane	C_6H_{14}
Heptane	C_7H_{16}
Octane	C_8H_{18}

A single atom of carbon can unite with 4 atoms of hydrogen, but 2 atoms of carbon can only unite with 6 instead of with 8, because in the latter case they would both be saturated with hydrogen and separated from each other, forming 2 molecules of marsh gas.

$$C_2H_8 = CH_4 + CH_4.$$

In ethane, on the contrary, the 2 atoms of carbon are only united with 6 atoms of hydrogen because they have mutually exchanged one unit of saturation. This requires explanation.

If we take two molecules of marsh gas, $CH_4 + CH_4$, and subtract from each of them an atom of hydrogen, we shall obtain two residues CH_3, in which the carbon atom would no longer be saturated. In losing H it has recovered a power of combination which renders it capable of again uniting with an atom of hydrogen, or of replacing an atom of hydrogen where one is wanting Now the affinity of the carbon atoms for each other leads them to interchange this force. We find them riveted together by the exchange of one unit of saturation, each accompanied by 3 atoms of hydrogen. Such is the meaning of the formula



$$H_3C-CH_3=H-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-H$$

in which this interchange of units of saturation is indicated by the strokes which separate the letters.[1]

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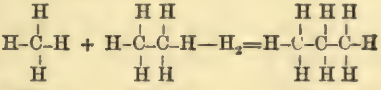
[1] This notation, now in general use, was employed for the first time in the lectures which I gave at the Collége de France during

This reasoning also shows that 3 atoms of carbon cannot combine with more than 8 atoms of hydrogen to form a saturated compound. In fact, if we take a molecule of ethane, C_2H_6, which is saturated, and a molecule of marsh gas, we must deprive each of them of an atom of hydrogen before the carbon of the one can combine with the carbon of the other. When this subtraction is accomplished there will only remain 8 atoms of hydrogen, and one of the carbon atoms of ethane, thus impoverished, will be able to unite with the carbon atom of methane, which has also been deprived of an atom of hydrogen.

The three carbon atoms of the new hydrocarbon, propane, will thus form a chain firmly riveted by the very affinities which would have separated them from each other. The following formulæ show the generation and the atomic grouping of propane :—



$$\mathrm{H{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}H + H{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}H - H_2 = H{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}H}$$

Methane. Ethane. Propane.

Before proceeding we must warn our readers against an error. Expressions of the kind of which we have just given an example are not intended to describe the position occupied by each atom in space. They indicate the relations which exist between the atoms. The pre-

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the summer of 1863, and were published first in Dr. Quesneville's *Moniteur scientifique*, and afterwards under the title of *Leçons de Philosophie chimique* (Hachette, 1864). This subject is discussed in pp. 140, 143, 145, 158 and 182 of this treatise.

ceding formula shows the manner in which the hydrogen atoms are divided between the three atoms of carbon, which are bound together by the interchange of units of saturation, thus forming, as it were, the nucleus or skeleton of the combination. The links of union inserted between the atoms do no more than mark their degree of saturation. They indicate the number and the interchange of the units of saturation, and that is all. Each atom of the quadrivalent carbon is surrounded by four strokes, while atoms of the univalent hydrogen have only one.

The line of argument which we have just been following applies also to saturated hydrocarbons containing a larger number of carbon atoms. Carbon atoms to the number of 4, 5, or 6 would interchange a part of the capacity of saturation which is inherent in them. It is clear that the carbon nuclei thus formed will only leave 10, 12, or 14 places vacant for as many atoms of hydrogen. Thus, to take a final example, 6 units of saturation are required by 4 atoms of carbon to form a firmly riveted chain, and of the 16 units of saturation which were contained in the 4 atoms of carbon there remain, therefore, only 10 capable of fixing atoms of hydrogen.

The above discussion will show the meaning and importance of Kekulé's great conception. This idea explains three facts, which have no apparent connection.

1st. The fact that no saturated hydrocarbon can contain a greater number of carbon atoms than that indicated of the formula C_nH_{2n+2}.

2nd. The fact upon which Laurent and Gerhardt had formerly laid so much stress—namely, that the number of hydrogen atoms contained in the hydrocarbons is always even.

3rd. The great stability of these hydrocarbons, which is due not only to the great affinity of hydrogen for carbon, but also of carbon for carbon.

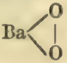
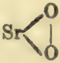
These facts, which were revealed by observation, only presented an empirical character. They are now explained by, and subordinated to, a principle from which they flow as natural consequences. The affinity of carbon for carbon is the cause of the infinite variety and immense number of carbon compounds: it is the essence of organic chemistry. No other element possesses in the same degree this ruling property of the element carbon, the faculty which its atoms possess of combining, of becoming riveted together, so as to form that framework, so variable in form, dimensions, and solidity, which acts, so to speak, as a support to the other elements, or rather to the atoms of the other elements. The latter are not, however, wanting in this property of uniting together, to which part of our subject we must now turn our attention.

IV.

We have described above the theory of diatomic gases and vapours. The molecules of hydrogen are formed of two atoms which, being univalent and combined with each other, have exhausted, by this act of union, all the capacity of combination which they possess. The molecule of hydrogen cannot, therefore, serve as a point of attachment to another atom; it represents a saturated compound which can only be modified by substitution. This is also the case with a molecule of chlorine, and when these two molecules are brought into contact with each other they are reciprocally decomposed, and hydrochloric acid is formed, as we have already seen, by the interchange of the hydrogen and chlorine atoms of these diatomic gases.

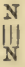
The molecule of oxygen, again, is formed of two atoms joined together, and as they each possess a capacity of saturation which is represented by two units, the union of the two atoms may be represented as cemented by the interchange of these two units of saturation or atomicities. Following the notation indicated above, this double exchange may be represented by two strokes. The molecules of oxygen may be written, therefore, $O{=}O = 2$ volumes. But we may also suppose these two atoms of oxygen to be simply united by a single unit of saturation: two out of these units are therefore left unsaturated, and it is clear that in this case a molecule of oxygen may serve as a point of attachment to other atoms, which may be fixed by each of the two atoms of oxygen. If $O{=}O$ represents a saturated couple, the symbol $-O-O-$ will represent a couple which is unsaturated and capable of attaching, for example, two atoms of hydrogen. This conception explains the constitution of hydrogen peroxide, $H-O-O-H$.

Certain peroxides have clearly the same constitution as hydrogen peroxide. This is the case with the peroxides of barium and strontium, which may be represented by the formulæ

 and 

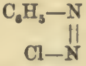
The considerations which we have just applied to bivalent oxygen apply equally to trivalent nitrogen. In free nitrogen we may consider that the two atoms of the molecule exchange the units of saturation which they possess, thus forming a solid chain which few elements have the power of disturbing or interrupting directly. It is well known that free nitrogen unites directly with a very few bodies.

This pair of nitrogen atoms $N \equiv N$ represents, from a thermal point of view, a more stable system (as having given rise to a greater liberation of heat) than a compound formed by an atom of nitrogen and, for example, three atoms of chlorine. But these two nitrogen atoms $N \equiv N$ which exchange 3 units of saturation, may only exchange 2 or 1 when, as in the preceding case, it acts as a point of attachment to other elements in complex combinations. The following are examples taken from those very remarkable organic combinations known as azo- and diazo-compounds :—



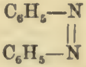
$$\begin{array}{c} N \\ ||| \\ N \end{array}$$

Free nitrogen.



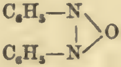
$$\begin{array}{r} C_6H_5-N \\ || \\ Cl-N \end{array}$$

Diazobenzene chloride.

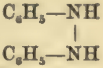


$$\begin{array}{r} C_6H_5-N \\ || \\ C_6H_5-N \end{array}$$

Azobenzene.



Azoxybenzene.



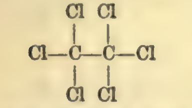
$$\begin{array}{c} C_6H_5-NH \\ | \\ C_6H_5-NH \end{array}$$

Hydrazobenzene.

We here see at once how the unsaturated pair of the two nitrogen atoms may serve as a support to other atoms, or as a point of attachment to their affinities, if we may make use of this figurative expression. We also see that it is not only elements such as chlorine, hydrogen, and oxygen which are capable of attaching themselves to the atoms of nitrogen (or others) which are unsaturated in their affinity, or which have not exhausted their capacity of combination; groups, such as phenyl, C_6H_5, given in the preceding formulæ, share this property with the elements. Phenyl can play the part and take the place of a certain atom of hydrogen, because it wants but one atom of hydrogen to become benzene. We shall return to this point presently.

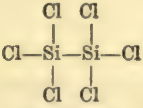
We have so far traced the origin, development, and consequences of this modern idea—namely, that the atoms of simple bodies can expend upon themselves a part or the whole of the *capacity of combination* which they possess. We must now enquire into the meaning of this term. We have observed this quality highly developed in the atoms of carbon; we have met with it again in hydrogen atoms, in oxygen and nitrogen atoms—that is to say, in the ordinary elements of organic compounds. We must now proceed to show that other simple bodies, such as silicon and the metals, also possess this property.

Silicon and titanium may be classed among the quadrivalent elements analogous to carbon. We are, in fact, acquainted with the tetrachlorides, $SiCl_4$ and $TiCl_4$. Friedel has succeeded in preparing a sesquichloride and sesquiiodide of silicon. The latter, the analogue of sesquichloride of carbon, C_2Cl_6, has the same constitution as ethane (p. 214). The two atoms of carbon being united together by the exchange of one unit of saturation, there only remain six which are, so to speak, free to take up six atoms of chlorine. In the sesquiiodide and sesquichloride of silicon the six atoms of iodine and chlorine play the same part, and the two atoms of silicon are united together, exchanging the fourth unit of saturation, or valency, which each of them possesses :—



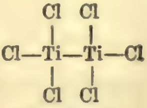
$$\begin{array}{ccccc} & \text{Cl} & & \text{Cl} & \\ & | & & | & \\ \text{Cl}- & \text{C} & - & \text{C} & -\text{Cl} \\ & | & & | & \\ & \text{Cl} & & \text{Cl} & \end{array}$$

Sesquichloride of carbon.



$$\begin{array}{ccccc} & \text{Cl} & & \text{Cl} & \\ & | & & | & \\ \text{Cl}- & \text{Si} & - & \text{Si} & -\text{Cl} \\ & | & & | & \\ & \text{Cl} & & \text{Cl} & \end{array}$$

Sesquichloride of silicon.



$$\begin{array}{ccccc} & \text{Cl} & & \text{Cl} & \\ & | & & | & \\ \text{Cl}- & \text{Ti} & - & \text{Ti} & -\text{Cl} \\ & | & & | & \\ & \text{Cl} & & \text{Cl} & \end{array}$$

Sesquichloride of titanium.

The sesquichloride of titanium shows an analogous composition. It must be remarked that the formulæ in question cannot be halved. The vapour density of all these bodies has been taken, and their molecular condensation must be expressed by the preceding formulæ.

The chlorides of iron and aluminium are analogous to the preceding chlorides. The result of the classical researches of H. Sainte-Claire Deville and Troost upon the vapour density of these chlorides has been to attribute to them the formulæ Fe_2Cl_6 and Al_2Cl_6; and we are forced to admit that the two atoms of iron and aluminium are united together in the same manner as the atoms of carbon, silicon, and titanium in the corresponding chlorides.

The couples Fe—Fe and Al—Al are, then, sexvalent. This ingenious idea is due to Friedel. Considering iron as quadrivalent in pyrites, FeS_2,[1] the eminent chemist regards the ferric compounds as containing two atoms of tetratomic iron united by the interchange of two units of saturation. In the couple (Fe—Fe), ferricum, there remain, therefore, only six free or disposable units of saturation. The violet chromic chloride, and perhaps the compounds which are called sesquichloride of osmium and ruthenium, have the same molecular constitution as the preceding chlorides.

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[1] The ferric tetrachloride corresponding to pyrites does not exist. The interpretation of this want lies in the fact that in the action

$[Al^{iv}—Al^{iv}]^{vi}Cl_6$
Chloride of aluminium.

$[Fe^{iv}—Fe^{iv}]^{vi}Cl_6$
Hexachloride of iron.

$[Cr^{iv}—Cr^{iv}]^{vi}Cl_6$
Hexachloride of chromium.

$[Os^{iv}—Os^{iv}]^{vi}Cl_6$
Hexachloride of osmium.

$[Ru^{iv}—Ru^{iv}]^{vi}Cl_6$
Hexachloride of ruthenium.

The corresponding oxides are—

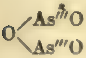
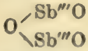
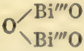
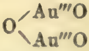
$$(Al_2)^{vi}O_3 \quad (Fe_2)^{vi}O_3 \quad (Cr_2)^{vi}O_3 \quad (Os_2)^{vi}O_3 \quad (Ru_2)^{vi}O_3.$$

These trioxides must not be confounded with the sesquioxides properly so called, which contain trivalent elements, such as arsenic, antimony, bismuth, and gold. These sesquioxides correspond to trichlorides, and the two atoms of metal which they contain are united, not directly with each other, but through an intermediary atom of oxygen.

of chlorine upon the protochloride a tetrachloride is not formed, because the affinity of iron for iron is greater than that of four atoms of chlorine for iron.

$$FeCl_4 + FeCl_4 = (Fe—Fe)^{vi}Cl_6 + ClCl.$$

We must add that important researches made by Scheurer-Kestner upon the ferric salt have confirmed the existence of sexvalent iron, Fe_2.

$As'''Cl_3$ Chloride of arsenic.	$Sb'''Cl_3$ Chloride of antimony.	$Bi'''Cl_3$ Chloride of bismuth.	$Au'''Cl_3$ Chloride of gold.
 $O\begin{cases}As'''O\\As'''O\end{cases}$ Arsenious anhydride.	 $O\begin{cases}Sb'''O\\Sb'''O\end{cases}$ Sesquioxide of antimony.	 $O\begin{cases}Bi'''O\\Bi'''O\end{cases}$ Sesquioxide of bismuth.	 $O\begin{cases}Au'''O\\Au'''O\end{cases}$ Sesquioxide of gold.

Iridium and rhodium also form well-characterised trichlorides and sesquioxides, which seem to belong to the preceding series; but they also form dichlorides, or rather tetrachlorides, in which we may admit the existence of couples (Ir—Ir) and (Rh—Rh) formed by the union of two atoms of iridium or two atoms of rhodium, which, having exchanged one unit of saturation, now possess only four atomicities.

$(Ir'''—Ir''')^{iv}Cl_4$ Dichloride of iridium.	$(Rh'''—Rh''')^{iv}Cl_4$ Dichloride of rhodium

As a final example of these unions which the atoms of the same element may form, by the partial exchange of their atomicities or units of saturation, we may mention the cuprous and mercurous compounds, of which the first contain two atoms of copper, the second two atoms of mercury, united together.

$(Cu''—Cu'')''Cl_2$ Cuprous chloride.	$(Hg''—Hg'')''Cl_2$ Mercurous chloride.
$(Cu''—Cu'')''O$ Cuprous oxide.	$(Hg''—Hg'')''O$ Mercurous oxide.

The formula which is here attributed to mercurous chloride has been amply justified (p. 115), whence it seems allowable to attribute an analogous composition to cuprous chloride, though here there is some uncertainty.

CHAPTER II.

I

Affinity and Atomicity, two Distinct Properties of Atoms.

We have in the preceding pages defined atomicity by regarding it as the saturating capacity of atoms, or as their valency in combinations. It is, then, a property inherent in the nature of atoms. We must proceed to show how it differs from affinity.

Affinity is the force of combination, chemical energy. It determines the intensity and the direction of chemical reactions, and is estimated by the thermal effects which these reactions produce. It varies essentially with different atoms. In combining with atoms of hydrogen, atoms of chlòrine, iodine, and bromine liberate very different quantities of heat; their affinity for hydrogen is very different, and is proportional to the quantities of heat liberated. But if we consider the combinations of the same elements with oxygen we shall find the order of affinities reversed. Chlorine is the element which possesses the weakest affinity for this body. The compounds of chlorine and oxygen are very unstable; some decompose with explosion—that is to say, are formed with absorption of heat. The affinity or chemical energy of a given body must therefore be considered as a relative property. It depends upon the nature of the element with which the one in question combines.

It depends also upon the conditions under which the bodies are placed. Berthollet long ago showed the influence which is exercised upon affinity by physical conditions, such as the degree of cohesion and the insolubility of bodies. This fact is too well known to require further remark (see p. 4); but we must remember how physical agents, such as heat, light, or electricity, can augment or diminish chemical energy, stimulate or retard the exercise of affinity. If mercury is heated to a certain temperature its atoms are in a condition capable of attracting atoms of oxygen. If the heat is increased the atoms of mercury and oxygen will be separated again. The affinity of mercury for oxygen is therefore subordinate to the temperature. It is a relative and not an absolute property, like the atomic weight. In the same manner a stream of electric sparks or the silent electric discharge can determine combinations between atoms which would have no action upon each other under ordinary conditions. Inversely, the same influences can produce decomposition, as is the case with the battery current. Here, again, the conditions in which the atoms are placed exercise a visible influence upon their affinities.

Atomicity is the capacity of saturation, or the value of substitution possessed by atoms, and this *valency* is an essentially different thing from the force of combination or the energy which resides in them. It governs the form of combinations, which varies with each atom. Thus the hydrogen combinations of chlorine, oxygen, nitrogen, and carbon have a different form (p. 211), and the atoms of carbon are so constituted that they can attract four atoms of hydrogen, whilst nitrogen can only attract three, &c. We should, moreover, observe that the force with which the hydrogen atoms are attracted by these different simple bodies is independent of the number of atoms fixed in each case. Thus we know that hydrogen combines with chlorine with extreme energy, oxygen combines with less force, carbon with difficulty and only when excited by most powerful influences, and nitrogen not at all directly.

These two notions, affinity and atomicity, which form the very foundation of the science, are therefore essentially different.

II

Atomicity a Relative Property of Atoms.

Let us pursue this parallel. Is the atomicity or capacity of saturation of every kind of atom immutably fixed, whatever the combinations may be into which they enter? By no means. The action of atoms must be regarded as reciprocal, so that in a compound formed of two heterogeneous atoms the properties of the one are influenced by those of the other, the two atoms adapting themselves, as it were, to each other. Atomicity is therefore a relative property, like affinity. This is easily proved to be the case. Nitrogen, phosphorus, arsenic, and antimony only combine with three atoms of hydrogen; the three latter elements also combine with three atoms of chlorine; but while phosphorus and antimony can unite with five atoms of chlorine to form the pentachlorides, arsenic can only unite with three atoms of this element. Here, therefore, we have essential differences in the saturating capacities of simple bodies for hydrogen and chlorine. The hydrogen compounds exhibit a particular form and belong to a certain type, the same for all; the chlorine compounds do not exactly correspond, phosphorus and antimony, but not arsenic, forming with chlorine chlorides which belong to a particular type.

Let us now consider some other compounds formed by the same group of bodies. We do not know of one of them forming a hydrogen compound or an ethyl or methyl compound belonging to the type RX_5; but nitrogen, which can fix neither five atoms of hydrogen nor five ethyl groups, is united in sal ammoniac to four atoms of hydrogen and one of chlorine, and in tetrethylammonium iodide to four ethyl groups and to one atom of iodine.

$$NH_3 + HCl = NH_4Cl;$$
$$NEt_3 + EtCl = NEt_4I.$$

Phosphorus, arsenic, and antimony also form the compounds—

PEt_4I
$SbEt_4I$

$AsMe_4Cl$
$AsMe_3Cl_2$
$AsMe_2Cl_3$
$AsMeCl_4$

which belong to the type RX_5.

The methyl compounds of arsenic are worthy of attention from our present point of view. Arsenic can neither combine with five atoms of chlorine nor with five methyl groups; but well-defined compounds are known containing for one atom of arsenic four methyl groups and one atom of chlorine, or four atoms of chlorine and one methyl group, whence it appears that the combining capacity of arsenic varies, and is in a manner increased when chlorine and methyl are *both* present to enter into combination with arsenic.

The oxygen compounds of the bodies in question belong generally to the types RX_3 and RX_5. But here again we meet with peculiarities worthy of notice. Nitrogen is bivalent in nitrogen dioxide, NO,[1] which compound is not saturated. It is quadrivalent in NO_2; but this latter, again, tends to unite with itself at a low temperature, thus forming the body $O_2N^v—N^vO_2$.

Arsenic forms with sulphur a compound AsS_2 or $As_2S_4 = S_2As^v—As^vS_2$, which has no analogue in the oxygen series.

We may conclude, therefore, that, as far as nitrogen and its congeners are concerned, there is no absolute rule for the saturating capacity of atoms, since we find that the latter varies with the nature of the elements or groups which are united with the simple bodies in question.

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[1] Or $—N'''O$.

Let us now consider the chlorine family. This body and its congeners behave towards hydrogen, ethyl, and the metals as univalent elements.

ClH hydrochloric acid.
$ClEt'$ chloride of ethyl.
ClK chloride of potassium.
Cl_2Pb'' chloride of lead.
Cl_3Sb''' chloride of antimony, &c.

This is not the case with the different oxygen compounds of chlorine and its congeners, in which the saturating capacity of these elements for oxygen is exhausted by degrees. Thus in hypochlorous acid, $Cl(OH)'$, chlorine is univalent; it is quinquivalent in chloric acid, $ClO_2(OH)$, and septivalent in perchloric acid,[1] $ClO_3(OH)$. With perchloric acid we may com-

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[1] Some time ago I expressed the idea that in certain oxygen compounds rich in oxygen the atoms of this body might be united in such a manner as to form a chain. Thus I represented the constitution of chloric acid and perchloric acid by the formulæ—

$Cl'O-O-O-(OH)'$	$Cl'-O-O-O-(OH)'$
Chloric acid.	Perchloric acid.

This hypothesis afterwards received support from ideas upon the constitution of the quinones. We know that Graebe and Liebermann regarded quinone as a benzene derivative, in which the diatomic group $(O-O)''$ was substituted for two atoms of hydrogen in benzene.

C_6H_6	$C_6H_4(O-O)''$
Benzene.	Quinone.

This idea had to be abandoned, and I must give up my old hypothesis upon the constitution of the acids of chlorine, sulphur, &c.

pare permanganic acid, $MnO_3(OH)$, where manganese is septivalent; it is bivalent in the dichloride $MnCl_2$, probably quadrivalent in the peroxide MnO_2, &c.

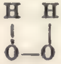
Iodine, which belongs to the family in question, presents a noticeable peculiarity; it forms with chlorine a protochloride, ClI, in which it appears to play the part of an univalent element, as in iodide of potassium, a saturated compound. In the protochloride the iodine is not saturated, for it can fix two more atoms of chlorine to form a trichloride. And this trichloride of iodine is unquestionably an atomic compound, for the three atoms of chlorine may be replaced by three acetyl groups (Schützenberger).

Thus we have the following compounds:—

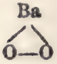
$I'Cl$	$I'''Cl_3$	$I'''(C_2H_3O_2)_3$
Iodine protochloride.	Iodine trichloride.	Iodine triacetate.

In iodic acid, $IO_2(OH)'$, iodine is quinquivalent; it

The existence of a chain of oxygen atoms in the higher acids of chlorine seemed scarcely to accord with the stability of these acids, increasing as it does in proportion to the number of oxygen atoms. I therefore incline to the idea that chlorine is heptatomic or septivalent in perchloric acid, and that sulphur is sexvalent in sulphuric acid. Given the fact of multiple proportions, if we admit that atomicity varies by degrees, there is no reason why we should not admit that a given element may manifest towards oxygen a capacity of combination seven times greater than towards hydrogen. We must, however, add that in certain peroxides analogous to hydrogen peroxide we must admit a similar existence of two atoms of oxygen united to each other.



Hydrogen peroxide.



Barium peroxide.

is septivalent in periodic acid, $IO_3(OH)'$. This latter acid forms very remarkable hydrates, and also corresponding definite salts.[1] These hydrates are—

$$IO_4H + H_2O = I^{vii}O_2(OH)_3;$$
$$IO_4H + 2H_2O = I^{vii}O(OH)_5.$$

The polyatomic character of iodine is much more striking than that of chlorine, and it is worthy of remark that iodine can fix in the different hydrates of periodic acid one, three, or five hydroxyl groups, forming relatively stable compounds.

Let us now pass to another family, that of oxygen, which is a bivalent element. Sulphur, selenium, and tellurium are also bivalent in their hydrogen compounds. They are quadrivalent in the anhydrides SO_2, SeO_2, TeO_2, and in the chlorides $SeCl_4$, $TeCl_4$; sexvalent in the anhydrides SO_3, SeO_3, TeO_3, and in sulphuric acid, $SO_2(OH)_2$, selenic acid, $SeO_2(OH)_2$, and telluric acid, $TeO_2(OH)_2$. Oxygen, which belongs to the same family, is one of the most strongly characterised bivalent elements. Can it, like its congeners, in some cases act as a quadrivalent element? This is not impossible, and the supposition receives support from an important discovery made by Friedel. Methyl oxide, $(CH_3)_2O$, will unite with hydrochloric acid, HCl, although both bodies may be regarded as saturated, and the combination is so stable that it is not completely dissociated at its boiling point. If the molecule $(CH_3)_2O.HCl$ can exist in the state of vapour

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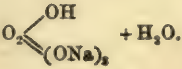
[1] Ordinary sodium periodate is



$IO_2\begin{cases} OH \\ (ONa)_2 \end{cases} + H_2O.$

the hypothesis of quadrivalent oxygen would account for this fact: chlorine and hydrogen can be attracted at the same time as the two methyl groups. (Friedel.)

The development of supplementary atomicities in oxygen would account, as Friedel has recently remarked, for the formation of certain compounds called molecular, notably for the fixation of water of crystallisation by a great number of anhydrous molecules. But this is connected with a general question which will be treated presently.

We may here draw attention to a remark which is not devoid of interest. Oxygen is bivalent; sulphur, selenium, and tellurium exhibit, in a great number of cases, higher atomicities. Again, in another family chlorine is univalent, at least as far as its combinations with hydrogen and the metals are concerned; iodine, however, manifests higher atomicities. Does it not seem as if this tendency to develope atomicities of a higher order might bear some relation to the increase of the atomic weight? for in the same family the heaviest elements seem more apt than the others to form combinations of a higher order—that is to say, to display higher atomicities.

Chromium possesses some analogy with sulphur, so much so that Mendelejeff places it, with molybdenum and tungsten, in the oxygen and sulphur group. In this metal the sexvalent character is even more pronounced than in sulphur; it becomes more so in molybdenum and tungsten, the atomic weights of which are higher, and which we know form hexachlorides. But the chlorine compounds of tungsten offer a striking example of the variation of atomicity in the same element. Not to mention the dichloride of tungsten, three other well-defined chlorides are known, namely—

$$WCl_4,$$
$$WCl_5,$$
$$WCl_6$$

in which tungsten evidently possesses a valency or combining value which differs as the numbers 4, 5, 6.

Let us consider some other metals from the present point of view—that is to say, of variable atomicity and of its tendency to augment in value with the increase of atomic weight.

Iron is bivalent in the dichloride, quadrivalent in the disulphide FeS_2 and in the hexachloride $(Fe—Fe)^{vi}Cl_6$ (Friedel); but the dioxide corresponding to the disulphide and tetrachloride is unknown—a fresh proof that atomicity is dependent upon the nature of the two combining elements.

Ruthenium[1] forms a well-defined tetrachloride, but the hexachloride of ruthenium is unknown. Such a combination is formed, however, by osmium, the analogue of ruthenium, the atomic weight of which is higher. We may add that in perruthenic acid and in osmic acid, which is so stable, ruthenium and osmium act as octovalent elements.

In the same manner we may compare rhodium to iridium, palladium to platinum; then again the alkaline metals to silver, to gold, and to thallium. We will confine ourselves to the latter comparison.[1] The alkaline metals and silver are univalent. Gold, the atomic weight of which is higher than that of silver, forms not only a protochloride, but also a well-characterised trichloride. It is the same in the case of thallium compared with cæsium and rubidium. With all these metals atomicities of a higher order are developed as the atomic weight increases.

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[1] Iron, ruthenium, and osmium form a series in Mendelejeff's table (pp. 159, 160).

Let us turn to carbon as a last example in this long discussion.

Following the example of Kekulé, we have considered carbon as quadrivalent in the saturated compounds which it forms with oxygen, sulphur, hydrogen, and chlorine. But there are other combinations of carbon, in which this element is not saturated. Carbon monoxide, $CO = 2$ volumes, furnishes an example. In this body carbon has not exhausted its capacity of combination for oxygen, since it can fix another atom to form carbon dioxide, CO_2.

Nor is its affinity or its combining energy exhausted in carbon monoxide, since this gas evolves heat when combining with oxygen; and yet carbon monoxide represents a stable molecule, a definite though unsaturated combination. It still retains an affinity for oxygen as an active force, without manifesting it as long as it remains carbon monoxide. This molecule differs both in form and type from that of carbon dioxide, and if we consider the units of saturation which are exchanged in the two combinations, we shall find that there are two in carbon monoxide and four in the dioxide. It follows, therefore, that in carbon monoxide the carbon atom plays the part of a bivalent element, while it is quadrivalent in carbon dioxide. This, however, is in reality but a figure of speech, for we may add that if it does not manifest to the full extent the capacity which it possesses for oxygen, it is not the less true that it possesses it, since it will manifest it as soon as occasion offers. Carbon monoxide contains an atom of carbon which is still in possession of two units of saturation, as may be expressed by the following formula: $=C^{iv}=O''$, carbon dioxide being $O''=C^{iv}=O''$.

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[1] The group of alkaline metals properly so called comprises the following metals:—

Li, Na, K, Rb, Cs,

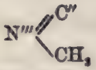
to which a sub-group may be added, comprising silver, copper, gold, and thallium. Copper seems misplaced here, and yet several reasons may be brought forward in favour of the connection of this metal with silver, amongst others the isomorphism of Cu_2S and Ag_2S (p. 141). As to thallium, we are evidently authorised in connecting it with the alkaline metals, although in Mendelejeff's table it is placed in another series.

It would be waste of time to propose and discuss the question of variable atomicity, if it could be reduced to these terms. But this is not the case. Cooper was the first to observe that carbon occurs in a great number of compounds in the condition of the carbon in carbon monoxide. It is important to examine into and establish this statement, for the highest aim of chemistry is to discover the constitution of bodies, to determine the grouping and mutual relations of atoms, to define, consequently, the part which each plays with regard to its neighbours; and if, amongst these atoms, there are some which have not exhausted their capacity of combination, they must be distinguished from the others and marked with a characteristic sign. This would be of great assistance in understanding constitutional formulæ and in interpreting chemical reactions, for it must not be forgotten that the properties of bodies are dependent upon their constitution.

Take, for example, the two isomeric bodies methyl cyanide and the methylcarbylamine of A. Gautier. Their composition is expressed by the formula C_2H_3N, which gives no information as to the causes of their isomerism. This is most satisfactorily explained by the rational formulæ proposed by Gautier—

$$N''' \equiv C^{iv} - CH_3$$

Methyl cyanide.



$$N''' \genfrac{}{}{0pt}{}{= C''}{- CH_3}$$

Methylcarbylamine.

The first represents a compound of cyanogen. The trivalent nitrogen exhausts its capacity of combination in exchanging three units of saturation with the quadrivalent carbon. The group (CN) is therefore univalent, for the carbon is not saturated. It is cyanogen, and can fix methyl by its unsaturated carbon. The methylcarbylamine is a base, an ammonia compound containing trivalent nitrogen. The latter exchanges one unit of saturation with a methyl group, and two units with an atom of carbon which here takes the place of two atoms of hydrogen. In fact, we might say that methylcarbylamine was derived from methylamine, in which the two hydrogen atoms are replaced by an atom of bivalent carbon. This is perfectly expressed by the term methylcarbylamine.

It is surely scarcely necessary to add that is not merely a theoretical view, but that the preceding formulæ interpret reactions, and are to a certain extent nothing more than the abridged and commodious representation of those reactions.[1]

We say, therefore, that carbon is contained in the two isomeric compounds in question under two different forms, quadrivalent in methyl cyanide, bivalent in methylcarbylamine, saturated in the former and, if you will, unsaturated in the second. And it is well to remember this, since the above notation serves to represent the constitution of bodies—that is to say, the reciprocal relations between atoms—and to interpret the accompanying reactions.

We must add a last example to the preceding, which we have chosen from a number of others.

Urea is an amide—that is to say, a derivative of ammonia—and the two atoms of nitrogen which it contains have the same value and are united to the same

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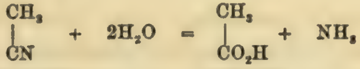
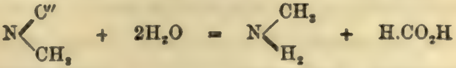
[1] Carbon is united to carbon in methyl cyanide. This body yields, by the action of potash, acetic acid, where carbon is united to carbon.



$$\begin{array}{c}CH_3\\|\\CN\end{array} + 2H_2O = \begin{array}{c}CH_3\\|\\CO_2H\end{array} + NH_3$$

Methyl cyanide. Acetic acid.

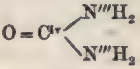
The two atoms of carbon are united to nitrogen in methylcarbylamine, and consequently separated from each other. They are also separated by the action of potash, the one remaining united to nitrogen in methylamine, the other giving formic acid.



$$N{<}\begin{array}{l}C''\\CH_3\end{array} + 2H_2O = N{<}\begin{array}{l}CH_3\\H_2\end{array} + H.CO_2H$$

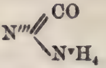
Methylcarbylamine. Methylamine. Formic acid.

atom of carbon; they are separated from each other, and are both trivalent. The isomer of urea, isocyanate of ammonium, contains nitrogen in two conditions: one atom, united to the carbonyl group, is trivalent; the other, which with four atoms of hydrogen forms the ammonium group, is quinquivalent. The following formulæ represent, therefore, the constitution of these two bodies, which can be transformed one into the other:—



$O=C^{iv}<^{N'''H_2}_{N'''H_2}$

Urea.



$N'''\lessgtr^{CO}_{N^{v}H_4}$

Isocyanate of ammonium.

In this case a change in the state of saturation of nitrogen accurately determines and explains the transformation of isocyanate of ammonium into urea, and of urea into isocyanate of ammonium.

III.

Now, what have we proved by the preceding remarks? We have endeavoured to establish that atomicity is not more immutable than affinity itself, but that it is a relative property of atoms. It varies, in fact, with the same element in the different combinations which the element is capable of forming with other elements, according to the nature of the latter, and in the combinations which it is capable of forming with the same simple body, according to the condition of saturation of the compound in question. It varies also with the temperature, for it is well known that, with regard to certain elements, certain forms of combination can only exist within very narrow limits of temperature.

These variations in the combining capacity of atoms are evidently a part of their intimate nature, of their form of existence. They probably depend upon the different velocities of the atoms. When two heterogeneous atoms come within their reciprocal spheres of action, they cannot unite unless their velocities are of a special character: there must be an accommodation, which is mutual. It determines the form of the combination, and also the form and dimensions of the new molecule in space. This is why the combining or saturating capacity of a given element is only a relative property; it cannot be the same towards the atoms of all elements, for each of the latter has its own individuality, its own velocity, which require a special character in that of the atom which enters into combination. The fundamental properties of the one, its chemical energy and capacity of combination, are influenced by the properties of the other in a manner which varies with the nature of the latter.

In the second place, it must be remembered that in the multiple compounds which one element forms with another, the state of saturation of the former varies. We are taught this fact by the law of multiple proportions. We know that the affinity of one element for another is exhausted by degrees, and these degrees accurately mark the state of saturation of the former. In this respect, then, the theory of atomicity is nothing more than the renewed and revived expression of the law of multiple proportions, as we remarked thirteen years ago.[1] Does this mean that the two conceptions are identical, and that the former shows no advance upon the latter, and is, in consequence, superfluous? Such an opinion would not be tenable for a moment. There is a great difference between the law of multiple proportions, which is only the direct expression of an experimental fact, and this studied theory, which consists in seeking for each simple body the forms of combination by which it is characterised, in comparing, in this respect, the elements with each other, in attributing to each of them a capacity of saturation which may vary in every compound, but which is perfectly definite in a given compound, in discovering the bearing of this property upon the constitution of chemical combinations, or how each atom exhausts in uniting with other atoms, whether of a different or *of the same nature*, the capacity of combination which it possesses, and in making use of these data to establish the probable relations between atoms in compounds, and, consequently, to construct the molecular edifice. This latter point is so important that we feel forced to return to it. But before closing the discussion now occupying our attention we must endeavour to explain a delicate point. Elements whose degree of saturation does not vary—such as hydrogen and, to a certain extent, the alkaline metals—are very easily characterised. They are univalent. This is not the case with those which form multiple compounds. Are phosphorus and nitrogen trivalent elements? They are so in the greater number and in the more stable of their compounds.

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[1] *Leçons de Philosophie chimique*, p. 221.

In others they are quinquivalent. This is the case with nitrogen in sal ammoniac, where it is united to five univalent elements, four of hydrogen and one of chlorine. And the very reason why ammonia can unite with hydrochloric acid is because the nitrogen which it contains is not saturated to its fullest extent. It is saturated as regards hydrogen, but not as regards hydrochloric acid.

The same difficulty arises with respect to phosphorus, arsenic, and antimony (see p. 227). It has been supposed at one time that these elements were trivalent, at another that they were quinquivalent. Setting aside the question as to what they are absolutely with regard to themselves, we may say that they act as trivalent elements in one order of compounds, and quinquivalent elements in other compounds. This is sufficient not only to determine the atomic structure of these compounds and of those which are derived from them, such as the acids of nitrogen, phosphorus, and arsenic,[1]

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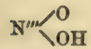
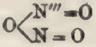
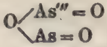
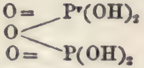
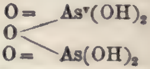
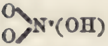
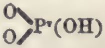
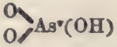
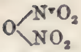
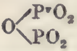
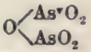
[1] The following examples are well calculated to show the practical utility of these considerations upon atomicity. The accompanying formulæ represent the composition of the two series of compounds mentioned in the text :—

$N'''H_3$ Ammonia.	$P'''H_3$ Phosphine.	$As'''H_3$ Arsine.
	$P'''Cl_3$ Trichloride of phosphorus.	$As'''Cl_3$ Chloride of arsenic.
$N'''(OH)_3$ Normal nitrous acid.	$P'''(OH)_3$ Phosphorous acid.	$As'''(OH)_3$ Normal arsenious acid (unknown).
 $N'''\begin{smallmatrix}\diagup O\\ \diagdown OH\end{smallmatrix}$ Nitrous acid (first nitrous anhydride)	"	"

but also to interpret the mode of formation and the reactions of all these bodies, which is the essential point.

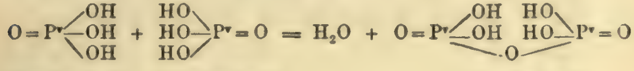
 Nitrous anhydride.	$P'''(OH)_3$ Phosphorous acid.	 Arsenious anhydride.
N^vH_4Cl Ammonium chloride.	P^vH_4I Phosphonium iodide.	As^vMe_4I Tetramethylarsonium iodide.
"	P^vCl_5 Phosphorus pentachloride.	As^vMeCl_4 Monomethylarsine tetrachloride.
$N^v(OH)_5$ Normal nitric hydrate (unknown).	$P^v(OH)_5$ Normal phosphoric hydrate (unknown).	$As^v(OH)_5$ Normal arsenic hydrate (unknown).
$O=N^v(OH)_3$ Orthonitric acid (unknown).	$O=P^v(OH)_3$ Orthophosphoric acid (first anhydride).	$O=As^v(OH)_3$ Orthoarsenic acid (first anhydride).
$O=N^v(O_3Bi''')$ Subnitrate of bismuth (orthonitrate)	 Pyrophosphoric acid (second anhydride).	 Pyroarsenic acid.
 Nitric acid.	 Metaphosphoric acid (third anhydride).	 Metarsenic acid.
 Nitric anhydride.	 Phosphoric anhydride.	 Arsenic anhydride.

We now understand the importance of the principles discussed in the text (p. 241). Without touching upon the question of the determination of the absolute saturating capacity of the atoms of nitrogen, phosphorus, and arsenic (and it is perfectly clear that they are relative), we simply take note of that which they manifest in a series of compounds, and make use of these data to establish relations of saturation between the atoms, and, to a certain extent, to account for the structure of molecules. It is very simple for the hydrogen and chlorine compounds; it becomes more complicated for certain oxygen derivatives. But we cannot fail to be struck with the light which the notation derived from considerations upon

It is evident from what has been said that we should encounter serious difficulties if we attempted to assign to each element a definite capacity of saturation, a fixed atomicity. In the case of certain polyatomic elements we should be embarrassed in our choice, for it is sometimes difficult to mark the limit of saturation.

atomicity throws not only upon the constitution, but also upon the mode of formation and upon the properties of these acids. Let us take a single example, the most complicated one.

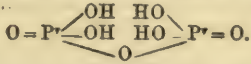
On moderately heating ordinary phosphoric or orthophosphoric acid, it is converted into pyrophosphoric acid. Now, the analysis of pyrophosphoric acid and the pyrophosphates shows that this acid only differs from orthophosphoric acid by half a molecule of water. The concurrence of two molecules of acid is therefore necessary for the formation of one molecule of water, and the residue of these two molecules remain united by an intermediary atom of oxygen, which suffices to saturate the phosphorus of the two molecules. This is expressed by the following equation:—



$$O=P^{v}\begin{cases}OH\\OH\\OH\end{cases} + \begin{matrix}HO\\HO\\HO\end{matrix}\Big\rangle P^{v}=O = H_2O + O=P^{v}\begin{cases}OH\\OH\end{cases}\begin{matrix}HO\\HO\end{matrix}\Big\rangle P^{v}=O \quad (\text{bridged by } O)$$

Orthophosphoric acid. Orthophosphoric acid. Pyrophosphoric acid.

The molecule of pyrophosphoric acid is therefore more complicated than that of phosphoric acid, and it is clear that it should be tetrabasic, as it contains four atoms of basic hydrogen. Thus the constitution, the mode of generation, and the fundamental properties of pyrophosphoric acid are clearly indicated by the formula



$$O=P^{v}\begin{cases}OH\\OH\end{cases}\begin{matrix}HO\\HO\end{matrix}\Big\rangle P^{v}=O.$$

The formulæ of phosphoric, pyrophosphoric, and phosphorous acids are founded upon considerations relative to the atomicity or valency of the atoms of phosphorus and oxygen. Now, I ask, could the law of multiple proportions, as it was understood some years ago, have given any information upon the atomic structure of all these molecules? Thus we were justified in our assertion that it was necessary to renew and revive this law to explain all these characteristics.

Nothing is easier for hydrogen, oxygen, boron, silicon, and a great number of metals. Hydrogen, the alkaline metals, and silver may be classed with the univalent elements; the alkaline earths—magnesium, zinc, copper, &c.—are bivalent. This estimation, however, does not apply to other elements, nor can they be characterised by their degree of atomicity, as the latter varies according to the degree and the nature of the combinations considered.

Those chemists who hold that atomicity is a fixed property of atoms, as invariable as their atomic weights, are guided by other considerations. They chose certain forms of combination, certain types which, more stable or more important than others, seem to them characteristic of a given element, and suitable for fixing its atomicity. Thus the type NX_3 has been taken as characteristic of bodies belonging to the nitrogen family; nitrogen and its congeners have therefore been regarded as trivalent. But here a difficulty arises. We know that the simple bodies in question have a great tendency to form more complicated compounds belonging to the type NX_5. What part, then, can they play in the latter compounds? They are, they say, trivalent, like the rest. In fact, they admit that the compounds NX_5 are not true atomic combinations, in which all the atoms are united so as to form a single molecule; they are divided, so to speak, into two groups, forming two distinct molecules combined together, $NX_5 = NX_3 + X_2$. Hence we have two kinds of combinations, atomic combinations, in which the molecule forms two volumes of vapour, and molecular combinations, in which one molecule is added to another molecule, and which, when they assume a gaseous form, occupy four volumes of vapour. This is the case with phosphorous pentachloride, with phosphonium iodide, with sal ammoniac, &c. This view has already been refuted. The combinations in question are true chemical compounds, and are merely dissociated and decomposed when heated (p. 111 *et seq.*)

There seems to me a difficulty in admitting that a chemical compound properly so called can be formed by the juxtaposition pure and simple of two molecules, which are attracted as such and preserve a sort of individuality after having contracted this union. Why does ammonia attract hydrochloric acid? Because the nitrogen which it contains is not saturated. This must be clearly understood. We admit that sal ammoniac, NH_4Cl, belongs to the type NX_5, and hold generally and implicitly that the chlorine and the four atoms of hydrogen are united individually to the quinquivalent nitrogen. But can chlorine give up its affinity for hydrogen and unite with nitrogen, which only has a slight attraction for it? This is a difficulty which was raised some time ago by Chevreul, and which appears to be increased by thermal considerations. The separation of chlorine and hydrogen should give rise to a considerable absorption of heat; the union of chlorine and nitrogen can only produce a feeble evolution of heat. The thermal result of the reaction should, therefore, be negative, and the formation of sal ammoniac should give rise to an absorption of heat. The contrary, however, takes place. This difficulty disappears if we admit that in ammonium chloride the affinity of the chlorine for hydrogen is satisfied not by its union with a certain atom of hydrogen, but by the attraction which it exercises upon all the atoms of hydrogen within the sphere of which it is now situated.

Ammonia combines at a low temperature with hydrochloric acid because a residue of energy and affinity is retained by the nitrogen, and perhaps also by the chlorine. This combination creates a new state of equilibrium between *all the elements*, producing a radiation, so to speak, of the atomic affinities and attractions of the atoms of nitrogen, hydrogen, and chlorine. This is the part played by affinity.

The atoms of hydrogen and chlorine unite with a great disengagement of heat, and seem to have exhausted their reciprocal affinity, and yet when the molecule of hydrochloric acid is placed within the sphere of action of the ammonia molecule there follows a fresh disengagement of heat. The reason of this is the following: the two molecules, free in their motions before combination, are not so afterwards; they are bound together, and henceforth execute their molecular and intermolecular motions with a certain intensity and in a definite manner, as a single system having a common centre of gravity. The fact of combination, therefore, produces in the end a loss of energy, and in this case, as in others, the final effect may be a resultant of many concomitant phenomena which are superposed—namely, variation of molecular energy and variation of atomic energy. This is the cause of the disengagement of heat.

Ammonia can unite with hydrochloric acid because the nitrogen atoms are so constituted, or, if you will, are animated by such motions, that they can admit into their system not only three atoms of hydrogen, but a fourth atom of hydrogen and an atom of chlorine, and that the motions of these five atoms can harmonise with those of nitrogen in a new system having a certain form and certain dimension in space. Such is atomicity.

We say, therefore, that hydrochloric acid can unite with ammonia for two reasons—firstly, because the atoms uniting are in possession of a residue of affinity; secondly, because the atoms of nitrogen can *admit* into their sphere of action a fourth atom of hydrogen and an atom of chlorine.

The difference between the two notions is evident from this example. We see also that we refer the faculty which ammonia possesses of attracting hydrochloric acid to a peculiar state, to a fundamental property of the atoms of the former. In admitting the existence of atoms we employ an hypothesis; our conception must embrace as much as possible to allow the deduction of all facts and to avoid the necessity of creating and employing secondary hypotheses. Chemical molecules are formed of atoms which attract each other. Such is the hypothesis. I know well that the atoms are invisible and inappreciable to the senses, and I do not believe that the direct proof of their existence and mutual attraction can ever be furnished. But this atomic attraction is only a form of universal attraction, and as an hypothesis equally legitimate. Why should we graft upon this hypothesis a second, a special attraction, which in a completed combination is exercised by one molecule upon another? It seems to us more probable that these so-called molecular combinations do not essentially differ from atomic combinations, and that the explanation lies in the properties of the atoms themselves.

IV.

This is a convenient place to introduce some developments of the subject of so-called molecular combinations.

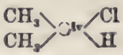
When calcium chloride is placed in water, an evolution of heat takes place, which indicates a chemical action. A combination has taken place, and the molecule of calcium chloride, which appears to us completely saturated, has nevertheless attracted one or several molecules of water. In my opinion this chemical action was not determined by the molecules of the calcium chloride and the water, but by the atoms contained in these molecules which were not saturated, or, in other words, which have preserved a residue of energy and a capacity of saturation which was not entirely exhausted. Hence they possess the power of exercising upon each other an action which is doubtless feeble, but sufficient to determine a chemical action. We maintain that the combination which has taken place, and which has given rise to a liberation of heat, is atomic. This heat could not proceed entirely from a loss of *vis viva* in the molecular motions, a loss which generally gives rise to physical changes, but also from a loss of *vis viva* in the intra-molecular motions—that is to say, in the atomic motions—which loss is the result and sign of chemical actions.

But the objection will be made that this idea supposes that the molecules which we regard as complete are not so, and that the atoms which we consider satisfied and saturated retain a residue of energy. This, in fact, is what must be admitted, for experience teaches us that it is very difficult to fix the absolute limits of saturation for an element, and especially a polyatomic element. The partisans of absolute atomicity meet with great difficulties when they characterise elements by the atomicity which is indicated by the limit of saturation —that is to say, by the maximum atomicity. This limit is not absolute, but varies with the conditions in which the element is placed and with the combinations considered.

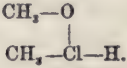
Are lead and manganese saturated in their dichlorides? This is improbable, for there is reason to believe in the existence of tetrachlorides—very unstable, it is true, and which only exist in an ethereal solution (Nicklès), but the ephemeral existence of which nevertheless proves that the atoms of manganese and lead can fix more than two atoms of chlorine.

We see that it is impossible to fix the limits of saturation with certainty for some elements at least, and it is no gratuitous hypothesis to suppose that the compounds which appear to us saturated, and in which chemical forces appear to be exhausted, still retain in some of their atoms sufficient energy to determine combinations.

Such is the idea, or rather hypothesis, which may be brought forward to explain the existence and formation of so-called molecular combinations. Thus in Friedel's chlorhydrate of methyl oxide we may assume that either the oxygen of the methyl oxide or the chlorine of the hydrochloric acid is still in possession of a residue of chemical energy. Assuming the oxygen to become tetravalent or the chlorine bivalent, the constitution of chlorhydrate of methyl oxide would then be represented by either of the following formulæ :—



or



$$\begin{array}{l} CH_3-O \\ \qquad\ \ | \\ CH_3-Cl-H. \end{array}$$

Similar considerations may be brought forward in order to explain the existence of a great number of complex combinations, double salts, and different combinations containing water of crystallisation. Chemical force is evidently called into play in the formation of these combinations, for they are formed in definite proportions and with liberation of heat. But, on the other hand, chemists have always supposed that we had here to deal with a peculiar kind of chemical compound. The force which fixes water of crystallisation upon sulphate of copper might perhaps, they said, be the same as that which brings sulphuric acid to act upon oxide of copper and which maintains the elements of the sulphate together, but it acts in a much weaker manner. In fact, in many chemical actions where affinity is exhausted by degrees this difference in the intensity of the forces is manifest. In phosphorus pentachloride and pentabromide two atoms of chlorine and bromine are retained more loosely than the other three. But how much more feeble the force must be which gives rise to the unstable combinations of phosphorus pentachloride with iodine chloride, or when the trichloride combines with four or even eight atoms of bromine, than the force which is called into play when phosphorus unites with three atoms of chlorine or bromine. The same observation also applies to the force which impels bromine to combine with ether to form the crystallised compound noticed by Schützenberger. We believe that it resides in the atoms themselves, and it seems most natural to attribute it, in the phosphorus compound in question, to the phosphorus, which can retain in the chloride or bromide PX_3 a residue of energy capable of fixing new atoms and of developing, if we may be allowed the expression, supplementary atomicities. But if, on the other hand, the compounds discovered by Prinvault are regarded as containing phosphorus, chlorine, and bromine, it does not appear improbable that the intervention of a third element should be necessary to maintain equilibrium between these complex and unstable molecules. One of the hypotheses by which we can make the theory of atomicity include all these facts consists, therefore, in attributing to bromine and iodine supplementary atomicities, which are developed, in some way, so as to unite all the atoms in the compounds in question.[1]

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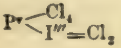
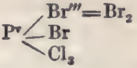
[1] Thus the constitution of the compounds PCl_6I and PCl_3Br_4 might be represented by the following formulæ :—



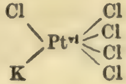
$$P^{v}\begin{cases} -Cl_4 \\ -I'''=Cl_2 \end{cases}$$

Two series of important facts still remain to be considered with this class of ideas—namely, the existence of double salts and that of compounds containing water of crystallisation. Can they be included in the theory of atomicity according to the principles just exposed for the 'molecular' combinations of phosphorus? This does not appear to be impossible. Take, for example, the double chloride of platinum and potassium. The chloride $PtCl_4$ marks the limit of saturation of platinum for chlorine: platinum is here quadrivalent. But we may suppose that it is not saturated. Though one



Formulæ analogous to the latter, in which figure several atoms of trivalent bromine, would explain the constitution of the compound PCl_3Br_4. These formulæ will appear improbable to many; I give them as pure hypotheses; but I beg permission to remark that we are here dealing with solid, unstable compounds, with crystals, and that the force which causes the formation of the latter is perhaps called into play in the aggregations of atoms: ($—I=Cl_2$, $—Br'''=Br_2$). I know that here we are treading on ground crowded with hypotheses. I grant, on the other hand, that formulæ of this kind are easily constructed, and that the notion of atomicity, thus extended to molecular combinations, is very elastic. More may be deduced from it. The facts which we are now discussing should follow from it as necessary consequences, as the constitution of the combinations of carbon and the interpretation of their numerous isomers follow as a natural consequence from the notion of quadrivalent carbon. It must be confessed that this is not so in the present case. I have, nevertheless, given the preceding formulæ, for it seemed to me that the idea of referring to the atoms themselves all the manifestations of chemical force is worthy of attention. It is a stepping-stone towards a more general hypothesis, which will allow the rational coordination and exact representation of all the intermolecular forces—chemical energy, atomicity, cohesion, force of crystallisation, and force of solution.

atom of platinum cannot unite with six atoms of chlorine (as osmium in $OsCl_6$), it can unite with five atoms of chlorine and one of potassium and form the double chloride



where it plays the part of a hexatomic or sexvalent element. This does not present any difficulty, for we merely admit a fact analogous to what we have remarked in connection with ammonia and other compounds—namely, that an atom of nitrogen cannot unite with five atoms of hydrogen, but that it can unite with four atoms of hydrogen and with one atom of chlorine. Our considerations upon molecular equilibrium in sal ammoniac also apply here.

Double salts generally contain one or more polyatomic metals; in every case they contain elements which are or can become polyatomic and thus exchange supplementary atomicities with similar elements of a second saline molecule (see Note I. in the Appendix).

As to water of crystallisation, we might admit with Friedel that it is attached to the salts by the supplementary atomicities of the oxygen, which tends to become quadrivalent. But this hypothesis, the development of which will be found in Note II. in the Appendix, we bring forward with reserve, and shall confine ourselves to a few short observations, upon this phenomenon of water of crystallisation, which is the extreme limit of physical and chemical actions.

We have admitted above that when calcium chloride is dissolved in water a chemical combination, properly so called, is formed. This salt unites, in fact, with water with evolution of heat, the combination *remaining dissolved in the water.* This is a chemical phenomenon; it is independent of the physical fact of crystallisation and of change of state. We know, in fact, from the ingenious experiments of Rüdorff[1] and Coppet[2] upon the crystallisation of saturated solutions, that the combination with water of crystallisation, passing in some manner the point of solidification, remains in solution. But, independently of this chemical phenomenon, which, like all others, obeys the law of definite proportions, there may be another fact to be observed—namely, a physical condition, a change of state which intervenes—crystallisation.

Crystalline form is undoubtedly connected with the atomic structure. In connection with this point we should notice the important work of Gaudin;[3] but before certain chemical molecules can assume certain crystalline forms we can well imagine that they must attract other molecules—water, for example, alcohol, or ether. And this aggregation of molecules must take place in definite proportions, the physical structure of the crystals only allowing the intervention of a definite number of molecules. This is the idea which Berthollet applied to combinations in general. The fixed proportions, he asserted, are determined by physical conditions of insolubility, change of state, and crystallisation. The fixed proportions, we assert, in these aggregations of molecules, which constitute crystals, are governed by the physical conditions and the geometrical necessities of crystallisation. The phenomena which give rise to these molecular aggregations are therefore both chemical and physical in nature, and are the continuation of the chemical phenomena properly so called.

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[1] Pogg., *Ann.*, t. cxiv. p. 63, 1861; t. cxvi. p. 55, 1862; t. cxlix.

[2] *Ann. de Chim. et de Phys.*, t. xxiii. p. 366, 1871; t. xxv. p. 502, and t. xxvi. p. 98, 1872.

[3] This work would have been more remarkable and more productive if Gaudin, instead of devoting himself exclusively to the idea of symmetry in molecules, had bestowed more attention upon chemical considerations, as he did so successfully some time ago with respect to the molecular constitution of silicon chloride and silica.

V.

The preceding remarks show the meaning which we attach to the notion of atomicity. We should be overlooking another feature of our subject if we did not draw attention to the fact that the changes in the saturating capacity of elements—that is to say, the increase in atomicity—are generally found to take place in a series either of even numbers or of uneven numbers. Without enumerating all the simple bodies, we may give the most striking examples of this fact.

Elements of Even Atomicity.

The increase of atomicity follows a series of even numbers in the elements belonging to the following groups :—

I. *Oxygen Group.*—Oxygen is bivalent. Sulphur, selenium, and tellurium are bivalent, quadrivalent, and sexvalent.

II. *Carbon Group.*—Carbon, silicon, titanium, zirconium, and tin are quadrivalent, or bivalent and quadrivalent.

III. *Groups of Metals of even Atomicity.*—Calcium, magnesium, zinc, iron, manganese: bivalent and quadrivalent. Chromium, molybdenum, and tungsten: bivalent, quadrivalent, and sexvalent. Platinum, palladium, &c.: bivalent, quadrivalent, sexvalent, and octovalent.

Elements of Uneven Atomicity.

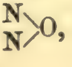
The increase in atomicity follows a series of uneven numbers in the elements belonging to the subjoined groups:—

I. *Hydrogen Group.*—Hydrogen, alkaline metals, silver, gold, and thallium: univalent and trivalent.

II. *Chlorine Group.*—Chlorine, bromine, and iodine: univalent, trivalent, quinquivalent, and septivalent.

III. *Nitrogen Group.*—Nitrogen, phosphorus, arsenic: trivalent and quinquivalent. Vanadium, antimony, bismuth, niobium, tantalum: trivalent and quinquivalent.

This distinction between the elements of even atomicity and those of uneven atomicity is not, for some elements at least, without importance. Why, amongst so many combinations of carbon and hydrogen, do we meet with none which contain an uneven number of hydrogen atoms? Because the atomicity of carbon is even, and the valency of its atoms in combinations is expressed by the numbers 2 and 4, never by the numbers 1 and 3. This is the case with carbon, and doubtless also for other elements, though it must be confessed that there are exceptions to this rule.

Nitrogen, univalent in the protoxide  $\begin{matrix}N\\N\end{matrix}\!>\!O$, is bivalent in the dioxide NO.

Chlorine, quadrivalent in the peroxide ClO_2, is quinquivalent in chloric acid, $ClO_2(OH)$.

Manganese, bivalent in $MnCl_2$ and in MnO, and sexvalent in potassium manganate, $MnO_2(OK)_2$, is septivalent in the permanganate $MnO_3(OK)$.

Tungsten, quinquivalent in the pentachloride WCl_5, is sexvalent in the hexachloride WCl_6.

Uranium, bivalent in the dichloride UCl_2, is trivalent in uranyl chloride, UOCl, and quinquivalent in the pentachloride UCl_5.

Vanadium, trivalent in the trichloride VCl_3, is quadrivalent in vanadyl dichloride, $VOCl_2$, and quinquivalent in vanadyl trichloride, $VOCl_3$.

The consideration with which we close this chapter —namely, the increase in atomicities—brings us back to our starting point—namely, multiple proportions. They are fundamentally considerations upon atomicity, and are the same facts which formerly guided Dalton in the statement of his law, and which at the present time lead us to attribute to elements combining values differing with the form of the compound in which they occur. Thus the notion of atomicity follows the direct interpretation of facts. It rests upon a solid foundation. In its turn it allows us to connect, interpret, and even foresee a great number of facts. It is therefore useful, because it is productive, and we shall retain it until it is lost in a more general notion embracing a greater number of facts.

CHAPTER III.

CONSTITUTION OF BODIES DEDUCED FROM THE THEORY OF ATOMICITY.

I.

We have endeavoured in the preceding pages to define the notion of atomicity, or the valency of atoms. It now remains to show that this notion lies at the base of all the partial theories which have been brought forward by chemists during the last fifty years, and especially to show how it accounts for the properties of those groups of atoms which we call radicals, and which have played so important a part in doctrines relative to the constitution of chemical compounds. There was a time when chemists could confine themselves to the consideration of radicals; in the written language of formulæ they were contented to represent them by distinct expressions, which were isolated from the other elements. They have now gone beyond this. Thanks to the indications furnished by ideas upon the saturation of atoms by each other—that is to say, by the theory of atomicity—they have succeeded in resolving these radicals, in discovering their mode of generation and their structure, and in determining in a plausible manner the connections which exist between atoms in combinations. This is the path which chemistry has recently followed, and how rapid has been the progress in this direction during the last twenty years! how many obscurities have vanished in the difficult problem of the intimate structure of chemical molecules, a problem the solution of which Gerhardt declared to be impossible! and, finally, what light has been thrown upon the question of isomerism, which has taken such an important position in chemistry! We must prove this before concluding.

Gerhardt's types expressed different forms of combination (p. 211). The hydrochloric acid type represented the combination of two univalent elements; the water type, the union of a bivalent atom with two univalent atoms; the ammonia type, the combination of a trivalent atom with three univalent atoms. These types, then, were not taken at chance; this conception was founded upon a profound idea, the form of which only has become antiquated, but which was fundamentally true, and which brought to light for the first time the differences between the combining capacities of elements. The very existence of the water type depends upon the combining capacity of oxygen, which requires for saturation two univalent elements, while chlorine only requires one. A single atom of oxygen can therefore fix not only two univalent atoms, but also groups of atoms which are one univalent atom short of saturation and the combining capacity of which is represented by that of this univalent atom. The number of these combinations, in which oxygen fixes two univalent atoms or residues, and acts as a kind of link between them, is very considerable; hence the richness of the water type. The same remarks apply to the ammonia type; it is therefore unnecessary to repeat them. We will merely remark that the brackets employed by Gerhardt, and which are still in general use, indicate that several elements or residues are united collectively to another element, an union or connection which is now expressed more clearly by strokes which mark the exchanges of units of saturation. The following symbols are therefore identical:—

Typical Formulæ.

$$\left.\begin{matrix}H\\H\end{matrix}\right\} = H\text{—}H$$

$$\left.\begin{matrix}H\\H\end{matrix}\right\}O = \begin{matrix}H\\H\end{matrix}\!>\!O \text{ or } H\text{—}O\text{—}H$$

$$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N = \begin{matrix}H\diagdown\\H\text{—}\\H\diagup\end{matrix}\!N$$

But to return to the residues or radicals which we have just mentioned. We have remarked that their substituting or combinating value is related to the state of saturation of the atoms.

Thus radicals composed of carbon and hydrogen are derived from saturated hydrocarbons by the loss of one, two, three, or four atoms of hydrogen, and we have seen how the theory of atomicity accounts for the state of saturation of the hydrocarbons of the series C_nH_{2n+2}(p. 213). These remarks may be extended to all chemical compounds. Their molecules may be considered as saturated when the combining capacities of their respective atoms are exhausted. Such molecules cannot increase by direct fixation of other atoms; they can only be modified by substitution. But when they are deprived of atoms or groups of atoms representing one, two, three, or four valencies or units of saturation, the residues acquire a combining capacity or a substituting value corresponding to the loss which they have experienced. They become, after this loss, univalent, bivalent, trivalent, or quadrivalent radicals. Below are some examples :—

Saturated Molecules.		Monatomic or Univalent Radicals.
Water, H_2O	—H	$=(OH)'$ hydroxyl.
Ammonia, NH_3	—H	$=(NH_2)'$ amidogen.
Methane, CH_4	—H	$=(CH_3)'$ methyl.
Hydrocyanic acid, HNC	—H	$=(CN)'$ cyanogen.
Ethane, C_2H_6	—H	$=(C_2H_5)'$ ethyl.
Benzene, C_6H_6	—H	$=(C_6H_5)'$ phenyl.
Alcohol, $C_2H_5\text{-}OH$	—H	$=(C_2H_5O)'$ oxethyl.
„ $C_2H_5\text{-}OH$	—H	$=(C_2H_4\text{-}OH)'$ hydroxethylene.
Acetic acid, $C_2H_3O\text{-}OH$	—H	$=(C_2H_3O\text{-}O)'$ oxacetyl.
Ethylene bromide, $C_2H_4Br_2$	—Br	$=(C_2H_4Br)'$ bromethyl.
Antimonyl chloride, SbOCl	—Cl	$=(SbO)'$ antimonyl.
Uranyl chloride, UOCl	—Cl	$=(UrO)'$ uranyl.
Acetic acid, $C_2H_3O\text{-}OH$	—$(OH)'$	$=(C_2H_3O)'$ acetyl.
Benzoic acid, $C_7H_5O\text{-}OH$	—$(OH)'$	$=(C_7H_5O)'$ benzoyl.
Nitric acid, $NO_2\text{-}OH$	—$(OH)'$	$=(NO_2)$ nitryl.
Nitrous acid, $NO\text{-}OH$	—$(OH)'$	$=(NO)'$ nitrosyl.
Glycollic acid, $C_2H_2(OH)'O\text{-}OH$	—$(OH)'$	$=(C_2H_2O\text{-}OH)'$ 1st univalent radical of glycollic acid.
Glycollic acid, $C_2H_2(OH)'O\text{-}OH$	—$(OH)'$	$=(C_2H_2(OH)'O)'$ 2nd univalent radical of glycollic acid.
Boric acid, $BO\text{-}OH$	—(OH)	$=(BO)'$ boryl.

Saturated Molecules.		Diatomic or Bivalent Radicals.
Ammonia, NH_3	—H_2	$=(NH)''$ imidogen.
Ethane, C_2H_6	—H_2	$=(C_2H_4)''$ ethylene.
Ethylene bromide, $C_2H_4Br_2$	—Br_2	$=(C_2H_4)''$ ethylene.
Carbon dioxide, CO_2	—O	$=(CO)$ carbonyl (carbon monoxide).

Saturated Molecules.		Diatomic or Bivalent Radicals.
Carbonyl chloride, $COCl_2$	$-Cl_2$	$=$ (CO) carbonyl (carbon monoxide).
Benzene, C_6H_6	$-H_2$	$=(C_6H_4)''$ phenylene.
Sulphuric acid, $SO_2(OH)_2$	$-2(OH)'$	$=(SO_2)''$ sulphuryl.
Oxalic acid, $C_2O_2(OH)_2$	$-2(OH)'$	$=(C_2O_2)''$ oxalyl.
Succinic acid, $C_4H_4O_2(OH)_2$	$-2(OH)'$	$=(C_4H_4O_2)''$ succinyl.
Glycollic acid, $C_2H_2(OH)O{-}OH$	$-2(OH)'$	$=$ $(C_2H_2O)''$ bivalent radical of glycollic acid (glycollyl).
Malic acid, $C_4H_6O_4$	$-H_2$	$=$ $(C_4H_4O_4)''$ fumaric and maleic acids.
Propylic alcohol, C_3H_8O	$-H_2$	$=(C_3H_6O)''$ allylic alcohol.

Saturated Molecules.		Triatomic or Trivalent Radicals.
Propane, C_3H_8	$-H_3$	$=(C_3H_5)'''$ glyceryl.
Phosphoryl chloride, $POCl_3$	$-Cl_3$	$=(PO)'''$ phosphoryl.

Saturated Molecules.		Tetratomic or Quadrivalent Radicals.
Ethane, C_2H_6	$-H_4$	$=C_2H_2$ acetylene.
Propane, C_3H_8	$-H_4$	$=C_3H_4$ allylene.
Tetrane, C_4H_{10}	$-H_4$	$=C_4H_6$ crotonylene.

Some of the radicals thus formed can exist in a free state; others cannot be isolated, combining, when nascent, with each other and doubling their molecule. The monatomic radicals which we have enumerated above must all be included in the latter category; not one exists in a free state. Hydroxyl, OH, does not exist; combined with itself it constitutes hydrogen peroxide, $H_2O_2 = HO{-}OH$. All attempts have as yet been unsuccessful to isolate double amidogen, $N_2H_4 = H_2N{-}NH_2$, but substitution derivatives of this body are known. It is well known that free cyanogen contains $C_2N_2 = NC{-}CN = 2$ volumes. As to methyl, the moment it is separated from iodine—for example, in methyl iodide—it doubles its molecule to form free methyl or ethane, $C_2H_6 = H_3C\text{–}CH_3 = 2$ volumes. The case is the same with ethyl, phenyl, and generally with all the radicals of saturated monatomic alcohols. The radicals of monobasic acids, such as acetyl and benzoyl, neither exist free nor in a state of double combination. On the other hand, Brodie has described, as peroxides of acetyl and benzoyl, compounds which may be regarded as resulting from the union of two molecules of oxacetyl or oxybenzoyl.

$(C_2H_3O\text{–}O)_2$ peroxide of acetyl.
$(C_7H_5O\text{–}O)_2$ peroxide of benzoyl.

As regards diatomic radicals, a great number of them exist in a free state. This is the case with ethylene and its homologues, with carbon monoxide or carbonyl, with sulphurous acid gas or sulphuryl, with nitrogen peroxide or nitryl, with nitrogen dioxide or nitrosyl. The tetratomic radicals, acetylene, allylene, and crotonylene, are known in a free state. We observe that all these bodies behave exactly like radicals in the sense which was formerly attached to this term; for are they not capable of combining directly with simple bodies, such as chlorine? The chlorides of carbonyl, sulphuryl, ethylene, and acetylene are formed by the direct union of chlorine with the isolated radicals, just as the metallic chlorides are formed by the direct union of chlorine with a metal. And ethylene fixes two atoms of chlorine, because its saturation is incomplete by two atoms of hydrogen. As to the oxygenated radicals, carbonyl and sulphuryl, they can fix not only two atoms of chlorine, but even an atom of oxygen to form the carbonic and sulphuric anhydrides CO_2 and SO_3. All this is too simple and too well known to require further remark. We will only add that the triatomic radicals containing carbon, such as glyceryl, (C_3H_5), do not exist in a free state. Free allyl or diallyl, $(C_3H_5)_2$, has doubled its molecule.

These are facts which we have just discussed. We must now show how they are accounted for by theory.

Carbon of even atomicity is united in all its combinations to a number of elements representing an even sum of units of saturation. This is why the groups CH_3 and CN do not exist separately. In these groups the three atoms of hydrogen and the atom of nitrogen represent an uneven number of units of saturation. They both require one atom of hydrogen to form the saturated combinations CH_4 and CNH; their combining or substituting value is equal, therefore, to that of one atom of hydrogen, and where an atom of hydrogen is wanting they can fill its place. They can also, by combining together, supply their mutual deficiency. In this manner are formed the compounds $H_3C–CH_3$ free methyl, NC–CN free cyanogen, $H_3C–CN$ methyl cyanide. But it is an important fact that the combination of these groups with each other is accomplished by the carbon atoms. These are the atoms which are not saturated in their affinities, which are mutually impelled towards each other in order to satisfy them. This is the new and essential point. The properties of the radicals are referred to the atoms themselves. Formerly they were considered as a whole. To the radical regarded as a whole was attributed the power of combining with or of being substituted for simple bodies. This was the fundamental point of view of Gerhardt's theory of types. We now go further. To discover and define the properties of radicals we go back to the atoms of which they are composed, and thus substitute a general hypothesis for a particular theory—namely, that the atomicity of radicals is subordinate to the atomicity of the elements. Thus methyl and cyanogen are monatomic or univalent radicals, because they contain the quadrivalent element carbon, which is not saturated. And this is the case also with radicals of higher atomicity. Why does carbonic monoxide act as a diatomic radical? Because the carbon which it contains is not saturated. Why, again, does ethylene, C_2H_4, fix two atoms of chlorine or bromine, thus acting as a diatomic radical? Because both the atoms of carbon which it contains are unsaturated; both can therefore directly fix other atoms, without breaking the link by which the two carbon atoms are riveted together.

But we must look more closely into the matter. Everything leads us to admit that in ethylene, C_2H_4, the two carbon atoms each attract two atoms of hydrogen, and that these two atoms of carbon, both of which are quadrivalent, can only satisfy the combining capacity residing in them by mutually exchanging *two* units of saturation, after having both fixed *two* atoms of hydrogen. We are thus forced to regard ethylene, and consequently analogous hydrocarbons, as containing two carbon atoms united by a double link—that is to say, by a double exchange of units of saturation—and this is the manner in which we must understand the formula $H_2C=CH_2=C_2H_4$, by which a great number of chemists represent the constitution of ethylene. But it may be objected that this is pure fiction, and that it would be simpler to admit that in ethylene carbon plays the part of a trivalent element, $H_2C{-}CH_2$, the two carbon atoms being united by a single exchange of atomicities. It is not a fiction, it is in accordance with facts, for we must not forget that all known hydrocarbons contain an equal number of hydrogen atoms. This would not be the case if carbon could play the part of a triatomic or trivalent element; if so, methyl, CH_3, and ethyl, C_2H_5, should exist in a free state. We must, therefore, conclude, taking experiment as our authority, that in the combinations of carbon and hydrogen carbon is never bivalent, as it is in carbon monoxide; methylene, CH_2, does not exist: that it is never trivalent; methyl, CH_3, and ethyl, C_2H_5, do not exist. It is therefore quadrivalent or tetratomic, and we are thus led to admit that carbon atoms have the faculty of exchanging with each other several units of saturation. But the combination thus constituted is in a state of unstable equilibrium, which is destroyed by the intervention of chlorine. The latter can fix itself upon molecules so formed, thus destroying the double link and constituting a perfectly saturated molecule. It is true that the affinity of carbon for carbon is strong; but when two atoms of this simple body have exchanged two units of saturation this affinity cannot stand, as far as the second bond is concerned, against that of chlorine, which tends to fix itself on to both the groups CH_2. The following formulæ will explain this view of the case :—

$C_2H_4 = H_2C{=}CH_2$ ethylene;
$C_2H_4Cl_2 = ClH_2C{-}CH_2Cl$ ethylene chloride.

Ethylene and analogous radicals have, therefore, the power of directly fixing chlorine and other elements, because they contain atoms of carbon, the combining capacity of which is not exhausted; since it is twice exerted between carbon atoms, it can still be manifested towards the atoms of chlorine. The latter severally fix themselves upon an atom of carbon in olefiant gas, although they refuse to unite directly with free carbon; the affinities of this body are, in fact, very different according as it is considered in the state of a simple compact and condensed body, C_n, or in a state of combination with hydrogen and in a gaseous form.[1]

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[1] It is a circumstance worthy of remark that chlorine or bromine, which do not unite with free carbon, as does oxygen, can fix themselves directly upon the unsaturated hydrocarbons, which oxygen cannot do. Are we to conclude that the chlorine is attracted, not by the carbon, but by the entire ethylene group acting as a radical, as was formerly supposed? This would be going a step backwards. In my opinion it is unquestionably the unsaturated carbon which attracts or admits the chlorine: it attracts it because it occurs in *gaseous* combination with hydrogen; it admits it because there are two vacant places in the system. The saturated hydrocarbon C_2H_6 also attracts chlorine; but, as there is no vacant place in the system, it can only admit it by losing two atoms of hydrogen. The hydrogen atoms seem, therefore, to exercise an influence upon the property possessed by carbon of fixing chlorine—that is to say, of admitting this element into its sphere of action. Such an influence is exercised in other instances and by other elements. Ethylene, which fixes chlorine, is incapable of directly fixing oxygen, but dibromethylene, $C_2H_2Br_2$, can fix it, according to Demole, to form the compound $C_2H_2BrO–Br$ (bromacetyl bromide). In this case, as in the former, the affinities of carbon have been modified by the intervention of other elements—hydrogen or bromine.

II.

The foregoing considerations upon the hydrocarbon radicals apply to all compounds capable of directly fixing elements, which compounds, in virtue of this property, resemble radicals. These elements are attracted by one or other of the unsaturated atoms contained by the compound in question. Let us take some examples.

Carbon monoxide can directly fix oxygen or chlorine because the bivalent carbon which it contains is not saturated. In carbonyl chloride and carbon dioxide the carbon has become quadrivalent. Like carbon monoxide, sulphurous acid gas can fix oxygen or chlorine, and it is the sulphur which attracts these elements. In sulphuryl chloride and in anhydrous sulphuric acid the sulphur has become sexvalent.[1]

Phosphorus trichloride, in fixing directly two atoms of chlorine, behaves, in some respects, like a radical, and it owes this property to the unsaturated phosphorus

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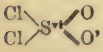
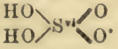
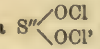
[1] Sulphurous acid gas being $S^{iv}O_2$ or $=S^{vi}O_2$, sulphuryl chloride is  $\begin{matrix}Cl\\Cl\end{matrix}\!>\!S^{vi}\!<\!\begin{matrix}O\\O\end{matrix}$, sulphuric acid  $\begin{matrix}HO\\HO\end{matrix}\!>\!S^{vi}\!<\!\begin{matrix}O\\O\end{matrix}$.

The formula  $S''\!<\!\begin{matrix}OCl\\OCl\end{matrix}$, which might be attributed to sulphuryl chloride, does not seem to us probable, since oxygen does not possess any tendency to unite with chlorine, and because the properties of sulphuryl chloride are not those of a body containing the hypochlorous residue OCl, which would decompose with explosion. We may add that selenium and tellurium are manifestly quadrivalent in the tetrachlorides and sexvalent in the anhydrides and selenic and telluric acids.

which it contains. The difference between the two views of the mode of action displayed by radicals is here shown in a most striking manner. It was formerly maintained that phosphorus pentachloride should be regarded as a combination of phosphorus trichloride with chlorine; the trichloride exists in it as a whole, as a radical endowed, as such, with a power of combination. We say now that the trichloride can take up chlorine because the phosphorus which it contains is not saturated; in the pentachloride phosphorus is united directly with five atoms of chlorine, and when phosphorus trichloride takes up two atoms of chlorine the latter are attracted by the unsaturated atom of phosphorus. When phosphene fixes hydriodic acid, or when ammonia unites directly with hydrochloric acid, they also act as radicals, and owe this property to the atom of phosphorus or of nitrogen which they contain, both of which show a tendency to become further saturated. In hydriodate of phosphene (phosphonium iodide), as in hydrochlorate of ammonia (ammonium chloride), they become quinquivalent.

In organo-metallic radicals properly so called we find properties of the same order, which we interpret in the same manner. And it must be confessed that these ideas upon the saturating capacity of elements, a capacity varying with the combinations in which they occur, are the natural consequence of the experiments undertaken twenty years ago upon the class of compounds in question. We refer to the classical discoveries of Frankland, Baeyer, Cahours, and the ingenious views which they introduced into science.

When Frankland compared with each other stannic iodide, stannethyl iodide, and stannic ethide, expressing the composition of these bodies by the formulæ

$$\mathrm{Sn}\left\{\begin{matrix}\mathrm{I}\\ \mathrm{I}\end{matrix}\right. \qquad \mathrm{Sn}\left\{\begin{matrix}\mathrm{C_4H_5}\\ \mathrm{I}\end{matrix}\right. \qquad \mathrm{Sn}\left\{\begin{matrix}\mathrm{C_4H_5}\\ \mathrm{C_4H_5}\end{matrix}\right.,^{1}$$

surely he showed by this notation that in these three bodies iodine and ethyl are combined in the same manner with tin, and that stannethyl, SnC_4H_5, only plays the part of radical because the tin which it contains tends to pass into the state in which it exists in stannic iodide. Stannethyl, SnEt, has just as much claim to be considered as a radical as stannous iodide, and in both cases it is the tin itself, and not the radical considered as a whole, which attracts the iodine.

And in his masterly statement of the theory of the saturation in the organo-metallic compounds of tin Cahours referred the power of attracting either chlorine, methyl, or ethyl, in order to attain a stable molecular equilibrium, to the tin itself, so that the general composition of all these saturated compounds might be expressed by the formula

$$SnX_4.^{2}$$

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[1] These formulæ are on the old notation : C = 6, Sn = 59.

[2] Cahours wrote Sn_2X_4. With the atomic weight of tin, Sn = 118, this expression becomes SnX_4, and the saturated compounds of tin receive, in consequence, the following formulæ :—

$SnCl_4$ = 2 vol. stannic chloride.
$SnEt_4$ = 2 vol. stannic ethide.
$SnMe_4$ = 2 vol. stannic methide
$SnEt_2Me_2$ = 2 vol. stannic dietho-dimethide.
$SnEtMe_3$ = 2 vol. stannic etho-trimethide.
$SnEt_3Me$ = 2 vol. stannic trietho-methide.

The condition of tin in these compounds differs, therefore, from that which it occupies in the stannous compounds SnX_2;[1] in the latter case it can attract elements or groups representing a combining value X_2, which it is incapable of doing in its saturated compounds.

The same remarks apply to arsenic in its methyl compounds; they belong to the two types AsX_5 and AsX_3. Now, Baeyer proved as early as 1858 that in the compounds of both series arsenic is united in the same manner to methyl and chlorine.

	Type AsX_5.		Type AsX_3.
$AsMe_4Cl$	tetramethyl-arsonium chloride.	$AsMe_3$	trimethylarsine.
$AsMe_3Cl_2$	trimethylarsine dichloride.	$AsMe_2Cl$	dimethylarsine monochloride.
$AsMe_2Cl_3$	dimethylarsine trichloride.	$AsMeCl_2$	monomethylarsine dichloride.
$AsMeCl_4$	monomethylarsine tetrachloride.	$AsCl_3$	arsenic trichloride.

This eminent chemist showed that the methyl compounds belonging to the type AsX_3 can directly fix Cl_2 and play the part of radicals. We say that this is the case because arsenic, trivalent in these compounds, tends to become quinquivalent in those in which it is saturated. And we see at once from this example that the limits of saturation are variable for each element, and subordinate to the nature of the simple bodies or groups with which

$SnEt_3Cl$ = 2 vol. stannic chloro-triethide (chloride of sesquistannethyl).
$SnEt_3I$ = 2 vol. stannic iodo-triethide (iodide of sesquistannethyl).
$SnMe_2I_2$ = 2 vol. stannic diodo-dimethide (iodide of stanno-dimethyl).

[1] Or $nSnX_2$.

this element is combined. Arsenic is saturated with chlorine in the trichloride as it is saturated with hydrogen in the trihydride. It is no longer saturated in the methyl compounds corresponding to the trichloride. The compounds $AsMeCl_2$, $AsMe_2Cl$, $AsMe_3$, can directly fix Cl_2.

There is, we think, no need to add further examples to those which we have already given. We have demonstrated and proved the fundamental point which we wished to bring forward—namely, that the properties of radicals capable of fixing other elements, after the manner of simple bodies, must be referred to the properties of the atoms contained in these radicals.

The same view must be extended to the residues or remains of various atomicity, which cannot be isolated as such, but of which the individual existence is admitted by the theory of radicals and types in organic compounds and in a great number of mineral compounds. Methyl, CH_3, ethyl, C_2H_5, acetyl, C_2H_3O, glyceryl, C_3H_5 (allyl), and many other analogous radicals do not exist; when we try to liberate them, they destroy themselves in combining with each other and doubling their molecule. The reason of this is that these radicals contain carbon, which is always of even atomicity; one of their carbon atoms, being combined with a sum of elements representing an uneven number of units of saturation, tends to complete this saturation. Thus CH_3 unites with H, or with Cl, or with OH, or with NH_2, or with CH_3, to form the following saturated compounds:—

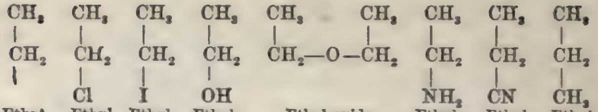
CH_3H	marsh gas (methyl hydride),
CH_3Cl	methyl chloride,
$CH_3(OH)'$	methyl hydrate,
$CH_3(NH_2)'$	methylamine,
$CH_3(CH_3)'$	free methyl or ethane.

In marsh gas the four atoms of hydrogen are united to the carbon in the same manner, and if we give to this body the name of methyl hydride it is simply to show that one of these hydrogen atoms—it matters little which—can be replaced by a chlorine atom or by a monatomic group. In methyl hydrate, $H_3C—O''H$, the carbon atom completes its saturation by uniting with an atom of oxygen; but, as the latter is bivalent, one atomicity remains free or disposable; it is satisfied by an atom of hydrogen. The same view may be taken of methylamine, $H_3C—N'''H_2$, in which the nitrogen saturates by one of its atomicities the carbon atom of the methyl, and by two others the two atoms of hydrogen. The two latter are not directly connected with the atom of carbon; they are united to the nitrogen atom, and, as it were, attached to it. In methyl oxide, $H_3C—O''—CH_3$, the bivalent oxygen completes the saturation of the two carbon atoms of two methylic groups. In free methyl or ethane, $H_3C—CH_3$, the two carbon atoms reciprocally complete their saturation.

Such is the new conception of radicals, a conception founded upon the atomicity of elements, and which is translated into notation by the preceding formulæ, the signification of which must now be intelligible to all. These formulæ, founded upon the theory of the reciprocal saturation of elements, allow the demonstration of the molecular structure of methyl compounds; they indicate the relations which exist between the several atoms composing the molecule ; they also express the mode of generation and the properties of the compounds in question.

In methyl hydrate, methyl oxide, and in methylamine the molecule is easily broken up : the oxygen and nitrogen are again separated from the carbon, the methyl group passing by exchange into other compounds. Thus, for example, hydrochloric acid easily converts methyl hydrate into methyl chloride, with formation of water. We have here a double decomposition, in which the radical passes intact from the hydrate into the chloride. This facility of exchange, which is exhibited by radicals in an immense number of reactions, was expressed most clearly by the typical notation. But it is a remarkable fact that this property does not extend to free methyl or ethane, since the carbon is firmly riveted to carbon, which explains, on modern ideas, the relative stability of this compound, a fact which caused so much surprise to chemists twenty-five years ago.

Let us go a step further in this direction, and now consider a radical containing two atoms of carbon—ethyl, C_2H_5. This is ethane minus an atom of hydrogen: one of the carbon atoms is united with only two atoms of hydrogen. It is the latter which is not saturated and which, to complete its saturation, can attract, as in the preceding case, an atom of hydrogen, chlorine, bromine, or a monatomic group.

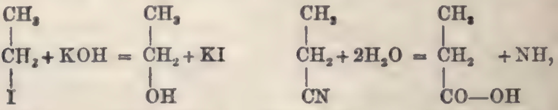


$$\begin{array}{cccccccc}
CH_3 & CH_3 & CH_3 & CH_3 & CH_3 \qquad\quad CH_3 & CH_3 & CH_3 & CH_3\\
| & | & | & | & | \qquad\qquad\quad | & | & | & |\\
CH_2 & CH_2 & CH_2 & CH_2 & CH_2{-}O{-}CH_2 & CH_2 & CH_2 & CH_2\\
| & | & | & | & & | & | & |\\
 & Cl & I & OH & & NH_2 & CN & CH_3
\end{array}$$

Ethyl. Ethyl chloride. Ethyl iodide. Ethyl hydrate. Ethyl oxide. Ethylamine. Ethyl cyanide. Ethyl methylide (propane).

In all these compounds we notice a part which is common to all, forming as it were the solid nucleus of the molecule, upon which are riveted, and as it were grafted, the various appendices. And in a great number of reactions this molecule will break up in such a manner that the appendices alone are removed, the nucleus remaining intact, and passing by exchange into another combination ; one ethyl compound is thus converted into another ethyl compound. This, however, is not always the case. Ethyl iodide and ethyl cyanide, though analogous compounds, do not behave in the same manner under the influence of potash : the former yields alcohol by double decomposition ; the latter propionic acid, a compound containing three atoms of carbon, like the cyanide itself.[1] Thus iodine is easily separated from the atom of carbon to which it is united, whilst the carbon atom of the cyanogen refuses to be separated. In this case it is as strongly united to carbon as the carbon atom of methyl in ethyl methide or propane. The strong affinity of carbon for carbon accounts for the diversity of these reactions, which was an enigma in the old theory

[1]



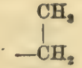
$$\begin{array}{llll}
CH_3 & & CH_3 & \\
| & & | & \\
CH_2 & + KOH = & CH_2 & + KI\\
| & & | & \\
I & & OH &
\end{array}
\qquad
\begin{array}{llll}
CH_3 & & CH_3 & \\
| & & | & \\
CH_2 & + 2H_2O = & CH_2 & + NH_3\\
| & & | & \\
CN & & CO{-}OH &
\end{array}$$

Ethyl iodide. Ethyl hydrate (alcohol). Ethyl cyanide. Propionic acid.

of radicals. This clearly shows the difference between the two points of view. In the old conception we have a group of atoms considered as a whole and united as such either to iodine or to cyanogen: in the modern conception, a group of atoms constituted in a certain manner and containing *a certain* atom of carbon united either to iodine or to cyanogen. In the former case the radical acts as a whole; in the latter it is resolved into different elements and exhibits its activity by one of its carbon atoms, which is not saturated.

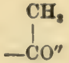
The case which we have just described is general. Hydrocarbon radicals analogous to ethyl can be resolved as we have just resolved this radical, the carbon atoms being united together and the hydrogen atoms unequally distributed amongst the carbon atoms. One of the latter will contain one less than it requires for saturation: this is the atom upon which other univalent elements or groups can fix themselves, by which the hydrocarbon group as a whole will act as a radical.

These ideas are applicable to the oxygen radicals derived from the former. Acetic acid contains such a radical: acetyl is ethyl modified by substitution.



$$\begin{array}{c} CH_3 \\ | \\ —CH_2 \end{array}$$

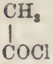
Ethyl.



$$\begin{array}{c} CH_3 \\ | \\ —CO'' \end{array}$$

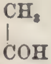
Acetyl.

In this oxygenised radical the atom of carbon combined with the oxygen appears in the same state of saturation as in ethyl, where it is united with two atoms of hydrogen. It is this carbon atom which fixes chlorine in acetyl chloride, hydrogen in aldehyde, hydroxyl in acetic acid, the group NH_2 in acetamide, and oxygen in acetic anhydride.



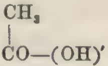
$\begin{array}{l}CH_3\\ |\\ COCl\end{array}$

Acetyl chloride.



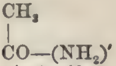
$\begin{array}{l}CH_3\\ |\\ COH\end{array}$

Aldehyde.



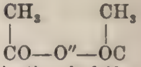
$\begin{array}{l}CH_3\\ |\\ CO—(OH)'\end{array}$

Acetic acid.



$\begin{array}{l}CH_3\\ |\\ CO—(NH_2)'\end{array}$

Acetamide.



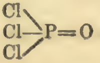
$\begin{array}{lcr}CH_3 & & CH_3\\ | & & |\\ CO & —O''— & OC\end{array}$

Acetic anhydride.

III.

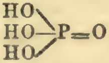
We have now made an important step, by showing how radicals can be resolved into definite atomic groups, in which we try to establish, by means of considerations founded on atomicity, the relations which exist between the atoms, the group acting as a radical whenever one or other of these atoms exists in an unsaturated state. It is evident that the formulæ which are developed according to the principles just explained, and which naturally increase in complication with the number of carbon atoms contained in the organic compound, do not represent the position of the atoms in space; being represented upon one plane, they cannot represent the form of a molecule which would occupy three dimensions in space. They only indicate, therefore, connections or, if you will, relations of juxtaposition. And these indications, incomplete though they are, are invaluable in a great number of cases. We must add, however, that attempts have been made to go a step further by forming hypotheses upon the geometrical structure of certain molecules and upon the probable grouping of atoms in space We shall say a few words upon this presently.

Radicals containing carbon are by far the most numerous in chemistry; they are not, however, the only ones, and it has long been impossible to consider as correct Liebig's definition—organic chemistry is the chemistry of compound radicals. The principles which we have just discussed may be applied to all groups acting as radicals, some of which we have enumerated on p. 262. Why does phosphoryl, the existence of which has been admitted in phosphoryl chloride, $PO.Cl_3$, and in orthophosphoric acid, $PO.(OH)_3$, play the part of a trivalent radical? Because it contains quinquivalent phosphorus. The latter has, by its union with oxygen, lost only two units of saturation; it has, therefore, three more to dispose of in some way, and these are represented in the chloride by three atoms of chlorine, and in phosphoric acid by three hydroxyl groups. In these bodies the single atom of phosphorus is therefore in connection (1st) with an atom of oxygen, (2ndly) with three atoms of chlorine or with the oxygen atoms of the groups OH. The formulæ



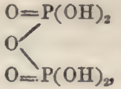
$$Cl_3{\equiv}P{=}O$$

and



$$(HO)_3{\equiv}P{=}O$$

express, therefore, the connections which exist between the different atoms in phosphorus oxychloride and in phosphoric acid. The latter enables us to conceive what takes place when phosphoric acid is dehydrated; in fact, the atomic constitution of pyrophosphoric acid and of metaphosphoric acid follows naturally from that of orthophosphoric acid. This point having been already developed in the note upon p. 243, we need not return to it here. We will merely remark that as far as pyrophosphoric acid,



is concerned, the intermediary atom of oxygen is connected with both the atoms of phosphorus. It is by this atom of oxygen that the two residues of the two partially dehydrated molecules of phosphoric acid are united to each other. It here plays the same part as the atom of oxygen in ethyl oxide (p. 276), where this atom rivets together the two ethyl groups, because it is united to the carbon of each group. We here see, from a striking example, with what facility the theories arising from an intelligent study of organic compounds may be applied to mineral compounds also. In this lies the character and the advantage of the theory of atomicity. It has cemented the alliance between inorganic and organic chemistry. It has given the key to the theory of radicals; it adapts itself perfectly to that of types; it binds together these two theories by subjecting them to a more general idea.

In the developed formulæ which we have given above the radicals are no longer represented as distinct groups, as if they had an individual existence. Such formulæ are acceptable from a theoretical point of view, and useful in a great number of cases. We must consider that, properly speaking, radicals do not exist as such in compounds. This is clearly demonstrated by the new notation, which shows that chemical compounds form a whole, and enables us to interpret a large number of reactions in which this whole, this molecular edifice, undergoes a more or less violent change. As soon as reactions become complicated Gerhardt's notation is no longer of service. It represented radicals by single expressions; it thus enabled us to represent in a striking manner reactions in which they are exchanged by double decomposition; it gave no information about those in which they are destroyed. Do we by this mean to say that we should entirely abandon this notation, so remarkable for its simplicity, for teaching purposes? By no means; condensed formulæ possess great clearness, and there are abundant reasons for their maintenance. Why should we not write alcohol $C_2H_5.OH$, ether $(C_2H_5)_2O$, ethylamine $C_2H_5.NH_2$, glycol $C_2H_4(OH)_2$, glycerine $C_3H_5(OH)_3$, nitric and metaphosphoric acids $NO_2.OH$ and $PO_2.OH$, and orthophosphoric acid $PO(OH)_3$? These formulæ are simple and sufficient in a great number of cases. They represent a certain number of reactions of which they are in a way the reflection. Is it not simpler and more convenient to represent amylic alcohol by the formula $C_5H_{11}.OH$, than by a formula developed in the following manner?

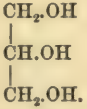
$$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}OH.$$

Amylic alcohol.

This formula, which represents normal amylic alcohol, only becomes useful when it is necessary to distinguish this alcohol from its isomers (see the note, p. 336). In all other respects the condensed formula stands good. We are here considering a relatively simple body; but if it were necessary to express by a developed formula the composition of ethal, $C_{16}H_{34}O$, or of stearic acid, $C_{18}H_{36}O_2$, or of cerotic acid, $C_{27}H_{54}O_2$, a whole page would not suffice. It is inconvenient in practice, for the eye has some difficulty in at once grasping these expressions, so widely spread upon the paper. It is, however, necessary to practise and to become accustomed to this exercise, for it is only by these formulæ that we gain an idea of the constitution of bodies, of molecular grouping, and cases of isomerism, facts which are essentially within the sphere of chemistry; for the properties of bodies and their reactions are unquestionably a function of this molecular grouping. This statement has often been made, and is in some sense a commonplace truth; but how great is the distance between this statement and even the demonstration which has been attempted within the last few years. The task was a difficult one, and had baffled the most ingenious and the most intelligent chemists with Gerhardt at their head. We have seen the means by which it has been possible to attack it, and how considerations relative to atomicity have led to the formation of hypotheses upon the grouping of atoms. That they are hypotheses must not be forgotten. Some are good, some are uncertain; and, in considering the formulæ by which we endeavour to represent the constitution of bodies, those only should be accepted which are the direct and established expression of facts: all others are without value. This is an important point; we shall, therefore, now endeavour to make it clear by pointing out the mode of construction, the exact meaning, and the real utility of the developed formulæ in question.

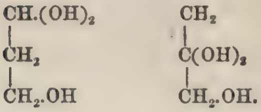
IV.

We will first consider a relatively simple compound, glycerine, which only contains three atoms of carbon These three atoms of carbon are united together, forming a group or nucleus which we meet with again not only in all the direct derivatives of glycerine, but also in the products of its decomposition or transformation, propylene, allyl alcohol, and acrolein. The constitution of the carbon nucleus of glycerine is represented in the developed notation by a chain of three carbon atoms riveted together. The atoms of hydrogen and oxygen are distributed among these carbon atoms in such a manner that each atom of carbon exchanges with the neighbouring atoms four units of saturation, and each atom of oxygen two. This is shown in the formula



$$\begin{array}{l} CH_2.OH \\ | \\ CH.OH \\ | \\ CH_2.OH. \end{array}$$

Another method of distribution of the atoms of oxygen and hydrogen between the carbon atoms is possible; but the number of these possible atomic arrangements is necessarily limited, from the fact that they must all satisfy the double condition that carbon is quadrivalent and oxygen bivalent. As examples of bodies possessing the composition of glycerine and a different atomic arrangement we may quote the following:—

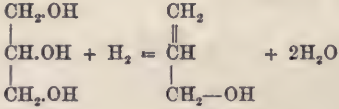


$$\begin{array}{l} CH.(OH)_2 \\ | \\ CH_2 \\ | \\ CH_2.OH \end{array} \qquad \begin{array}{l} CH_2 \\ | \\ C(OH)_2 \\ | \\ CH_2.OH. \end{array}$$

These bodies would be isomers of glycerine, the existence of which is foreseen by theory. They are unknown, and we must add that there is little probability of their existence in a state of liberty, because those compounds in which one atom of carbon is united to two OH (hydroxyl) groups have but little stability.[1]

The above construction of the formula of glycerine accounts for the properties and transformations of this body. Let us take two examples. Nothing is easier than to represent the transformation of glycerine into allyl alcohol and into trichlorhydrin.

The first reaction is expressed by the following equation :—



$$\begin{array}{l} CH_2.OH \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array} + H_2 = \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2{-}OH \end{array} + 2H_2O$$

Glycerine. Allyl alcohol.

But allyl alcohol is not a saturated compound; it is capable of directly fixing bromine, hydrobromic acid, &c. The preceding formula expresses this fact, by showing that two atoms of carbon exchange with each other two units of saturation and are riveted together

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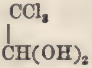
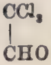
[1] Thus chloral hydrate

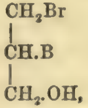


$\begin{array}{l} CCl_3 \\ | \\ CH(OH)_2 \end{array}$ is easily decomposed into chloral



$\begin{array}{l} CCl_3 \\ | \\ CHO \end{array}$ and water.

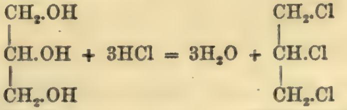
by a double bond. This is indicated by the double connecting bond. It is suppressed in the additive product



$$\begin{array}{l} CH_2Br \\ | \\ CH.B \\ | \\ CH_2.OH, \end{array}$$

dibromopropyl alcohol (allyl-alcohol bromide), which is the result of the direct action of bromine upon allyl alcohol.

When glycerine is transformed into trichlorhydrin by the successive action of hydrochloric acid and phosphorus pentachloride, the three OH groups are replaced by three atoms of chlorine—



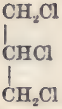
$$\begin{array}{l} CH_2.OH \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array} + 3HCl = 3H_2O + \begin{array}{l} CH_2.Cl \\ | \\ CH.Cl \\ | \\ CH_2.Cl \end{array}$$

Glycerine. Trichlorhydrin.

We see that in trichlorhydrin each atom of carbon is connected with an atom of chlorine, and this distribution of the chlorine atoms is characteristic of trichlorhydrin. A different distribution would imply a different atomic arrangement, and bodies thus constituted, though formed of the same atoms as trichlorhydrin, and possessing, consequently, the same composition and the same general formula, will be isomeric and not identical with trichlorhydrin. These isomers exist. Their existence is foreseen, their number limited, and their constitution indicated by theory. This must be proved, for it is the whole point of the question.

Given three atoms of carbon united together and possessing eight units of saturation, we proceed to distribute amongst these three carbon atoms five atoms of hydrogen and three atoms of chlorine, in such a manner as to attribute to each carbon atom four valencies or units of saturation. There are five different ways of satisfying this condition, and, consequently, theory can predict the existence of only five bodies presenting the composition of trichlorhydrin. Their molecular structure is expressed by the following formulæ :—

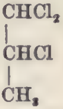
I.



$$\begin{array}{l}\mathrm{CH_2Cl}\\|\\\mathrm{CHCl}\\|\\\mathrm{CH_2Cl}\end{array}$$

Trichlorhydrin; boiling point 158°.

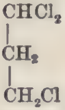
II.



$$\begin{array}{l}\mathrm{CHCl_2}\\|\\\mathrm{CHCl}\\|\\\mathrm{CH_3}\end{array}$$

Boiling point 140°.

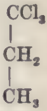
III.



$$\begin{array}{l}\mathrm{CHCl_2}\\|\\\mathrm{CH_2}\\|\\\mathrm{CH_2Cl}\end{array}$$

Unknown.

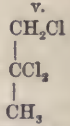
IV.



$$\begin{array}{l}\mathrm{CCl_3}\\|\\\mathrm{CH_2}\\|\\\mathrm{CH_3}\end{array}$$

Unknown.

V.



$$\begin{array}{l}\mathrm{CH_2Cl}\\|\\\mathrm{CCl_2}\\|\\\mathrm{CH_3}\end{array}$$ [1]

Methyl-chloracetol chloride; boiling point 123°.

Two of these bodies have not yet been obtained; but we have learnt from frequent experience that gaps of this kind may be filled up, and we could quote cases

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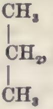
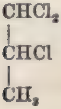


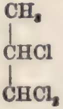
[1] The hydrocarbon $\begin{array}{l}\mathrm{CH_3}\\|\\\mathrm{CH_2}\\|\\\mathrm{CH_3}\end{array}$, the type of combination from which all these chlorine compounds are derived, possessing a symmetrical structure, the number of these derivatives is limited to five, because the substitutions effected in one of the groups CH_3 are equivalent to those effected in another group CH_3.

Thus the following chlorine derivatives must be regarded as identical :—

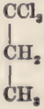


$$\begin{array}{l}\mathrm{CHCl_2}\\|\\\mathrm{CHCl}\\|\\\mathrm{CH_3}\end{array}$$

identical with

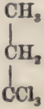


$$\begin{array}{l}\mathrm{CH_3}\\|\\\mathrm{CHCl}\\|\\\mathrm{CHCl_2}\end{array}$$



$$\begin{array}{l}\mathrm{CCl_3}\\|\\\mathrm{CH_2}\\|\\\mathrm{CH_3}\end{array}$$

identical with

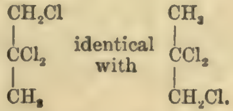


$$\begin{array}{l}\mathrm{CH_3}\\|\\\mathrm{CH_2}\\|\\\mathrm{CCl_3}\end{array}$$

more complicated than that under discussion where the attempt has been most successful;[1] and it is an important fact that, if we except cases of purely physical isomerism and those in which dimorphism comes into play, no case of chemical isomerism has as yet been observed which would not agree with those predicted by theory. We have here a striking confirmation of the theory which limits the number of possible isomers by considerations relative to atomicity or to the reciprocal saturation of atoms. Without these considerations a far larger number of isomers might be deemed possible.

Thus, to return to the preceding case, given three atoms of carbon, five atoms of hydrogen, and three atoms of chlorine, if it were merely a question of distributing the atoms of hydrogen and chlorine amongst the atoms of carbon, the numbers of possible arrangements between these different would be very considerable, and easily calculated by the rules of algebra.

A celebrated chemist, Berthelot, has been guided by peculiar considerations in theoretical predictions relative to the number of possible isomers in a given case. He admits that the same body may yield different isomers,



$$\begin{array}{l} CH_2Cl \\ | \\ CCl_2 \\ | \\ CH_3 \end{array} \quad \begin{array}{c} \text{identical} \\ \text{with} \end{array} \quad \begin{array}{l} CH_3 \\ | \\ CCl_2 \\ | \\ CH_2Cl. \end{array}$$

The identity of the bodies in question will at once be seen when we observe that their formulæ are simply reversed.

[1] The isomers of amylene will be mentioned presently, and in Note III. (p. 336) the isomers of amyl alcohol.

according to the manner in which it has been formed. Thus propyl hydride or propane may be formed in different ways—namely, by the addition of two atoms of hydrogen to propylene, or by the addition of methane to ethylene, or again by the addition of methane to ethane with a loss of two atoms of hydrogen.[1] If now in this hydrocarbon, propane, three atoms of chlorine are substituted for three atoms of hydrogen, the compounds formed may differ, in the first place, according to the manner in which the propane acted upon has been formed; in point of fact, says Berthelot, propane may contain different residues, according to the nature of the generating hydrocarbon. In the second place, it may yield distinct isomers, according to the part which is played in it by these residues. This point, again, may produce differences in the trichlorinated derivatives. They may differ, finally, according to the order in which the substitution has been effected. Thus, supposing three atoms of hydrogen to be successively replaced by three atoms of chlorine, the trichlorinated compounds thus formed may differ according to the order of succession in which these hydrogen atoms have been replaced.

Several objections may be raised against these theoretical views. In the first place, we cannot admit that a difference in the mode of formation should be a sufficient reason to determine isomers. In fact, bodies of

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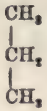
[1] $$\begin{aligned} C_3H_6 + H_2 &= C_3H_8, \\ CH_4 + C_2H_4 &= C_3H_8, \\ CH_4 + C_2H_6 - H_2 &= C_3H_8, \\ 3CH_4 - 2H_2 &= C_3H_8. \end{aligned}$$

the same composition having a different origin may be identical; they can only be regarded as isomers when it can be proved that they possess different properties.

In the case before us, propane, whatever its mode of formation, is one and the same body, and, before admitting that it can give rise to particular isomeric derivatives by the mere fact of difference in the methods of its formation, it would be necessary to show that it receives from the latter, in each case, particular properties, pointing to a difference of constitution. In a word, it would be necessary to prove that bodies formed by different reactions are isomeric.

This may happen in certain cases; in the particular case which we are discussing it is not so, for there is nothing to show that propanes formed in different ways differ from each other in their structure, or, as Berthelot expresses it, in the residues which they contain. In trying to discern the residues of generating hydrocarbons in a complex hydrocarbon, Berthelot endeavours to determine the molecular structure of the latter. Further, in chlorine derivatives he marks the place of chlorine in each of these residues. He constructs constitutional formulæ from the modes of formation of the hydrocarbons. Nothing is more legitimate in principle; but, unfortunately, the reactions which he takes as examples are not those from which any certain conclusion upon the constitution of bodies can be deduced: they are due to the action of heat, the most powerful form of reaction.

Passing to another point, what is the meaning of this expression, 'generating hydrocarbons'? It is far from expressing a definite idea. Also is it not a gratuitous supposition to admit that one chlorinated body can differ from another chlorinated body solely according to the order in which the substitution has been effected? Doubtless, when we substitute for several atoms of hydrogen different elements or groups—for example, chlorine and bromine, or chlorine and nitryl residues, NO_2—the order of substitution is by no means an indifferent matter, because it is not a matter of indifference which place is occupied by chlorine or bromine, or by a nitryl residue; but when all the places are occupied by chlorine, it matters not whether this or that place is occupied first. In any case the contrary supposition requires proof. Upon this subject Berthelot has accumulated hypotheses with an ingenious fecundity which in the present case has produced a remarkable result. The eminent chemist admits the possible existence of several hundred trichlorhydrins from a consideration of the relative order of reactions.[1] We say that there are five. Where is the sixth? In the case of propane or propyl hydride we maintain that no isomers are predicted by theory. Between three atoms of carbon and eight atoms of hydrogen there is but one possible arrangement—two groups of CH_3 united to one group of CH_2, as shown in the formula



$$\begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ CH_3 \end{array}$$

This formula is founded upon the consideration that the carbon atoms are quadrivalent, and that they can interchange a portion of their capacity of saturation. It is in this manner that the theory of atomicity predicts, interprets, and limits the number of isomers; it has furnished the elements of one of the greatest advances which science has accomplished in the last twenty years. It was generally said that isomerism is due to the difference in molecular grouping. This was stating the problem; the next thing was to solve it. The theory of atomicity has successfully attacked the problem by introducing into the discussion exact data, which have been in a great number of cases confirmed by experiment.

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[1] *Bulletin de la Société chimique*, nouv. sér., t. xiii. p. 402.

V.

This point is so important that I must ask permission to demonstrate by a fresh example the considerations by which chemists are now guided in the interpretation of isomers, and generally in conceptions relative to the constitution of bodies.

Let us take a hydrocarbon which has been the subject of a great number of experiments, amylene.

This body contains five atoms of carbon and ten atoms of hydrogen, two less than the saturated hydrocarbon of the series, amyl hydride or pentane, C_5H_{12}. Starting from the idea of the quadrivalence of carbon, theory predicts at least eight possible arrangements of the five carbon atoms and the twelve atoms of hydrogen. In the first place, the latter may be equally divided among the former, so that each atom of carbon, riveted by two atomicities to its neighbours, is combined with two atoms of hydrogen.[1] There is every reason to believe that amylene thus constituted does not exist, and that this is also the case with those in which three or four carbon atoms present a similar arrangement. It should be remarked that bodies thus constituted would be in a manner saturated, all the units of saturation belonging to the five carbon atoms being employed either in fixing hydrogen or in uniting the atoms of carbon. Now, all known amylenes[2] present the

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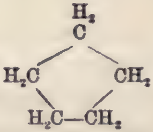
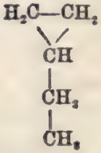
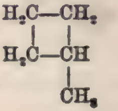
[1] On this hypothesis, which recalls Kekulé's celebrated hypothesis upon benzene, the atoms of carbon would form a ring, or closed chain, and the constitution of amylene, which would be the true homologue of ethylene, would be expressed by the following formula:—



We can conceive, further, the existence of two amylenes in which three or four carbon atoms would form a closed chain, two atoms, or a single atom, of carbon forming a kind of appendix, as may be observed in the hydrocarbon derivatives of benzene. The following formulæ would express the constitution of these amylenes:—

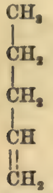




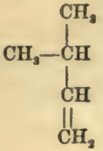
[2] The five amylenes in question present the following constitution:—

character of non-saturated compounds: they absorb bromine with energy, a property which is easily accounted for theoretically by supposing that two of the carbon atoms which they contain exchange not one unit of saturation, but two, as is shown by the formulæ given in the note below, which express the constitution of five different amylenes. In these formulæ the double bonds between two contiguous carbon atoms are represented by a double bond, a most convenient form of notation, as it enables us to show at once the state of saturation of each atom of carbon.

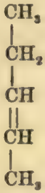
When an amylene thus constituted fixes two atoms of chlorine and bromine, or one molecule of hydro-


$\begin{matrix}CH_3\\ |\\ CH_2\\ |\\ CH_2\\ |\\ CH\\ \|\\ CH_2\end{matrix}$

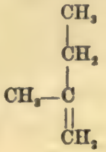
Ethyl-allyl; boiling point 40° (?).



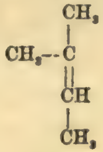
Flavitzky's amylene; boiling point 21°.


$\begin{matrix}CH_3\\ |\\ CH_2\\ |\\ CH\\ \|\\ CH\\ |\\ CH_3\end{matrix}$

Boiling point 38°–40°.

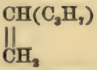


Amylene derived from active amylic alcohol (Le Bel); boiling point 32°.

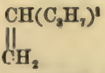


Ordinary amylene; boiling point 36°.

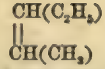
We may regard them as substituted derivatives of ethylene, $\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix}$, in which one or several atoms of hydrogen are replaced by various alcohol radicals. This conception enables us to express their constitution by relatively simple formulæ, which we give in the same order as above:—


$\begin{matrix}CH(C_3H_7)\\ \|\\ CH_2\end{matrix}$

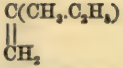
Propyl-ethylene.


$\begin{matrix}CH(C_3H_7)^1\\ \|\\ CH_2\end{matrix}$

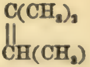
Isopropyl-ethylene.


$\begin{matrix}CH(C_2H_5)\\ \|\\ CH(CH_3)\end{matrix}$

Normal ethyl-methyl-ethylene.


$\begin{matrix}C(CH_3.C_2H_5)\\ \|\\ CH_2\end{matrix}$

Methyl-ethyl-ethylene.


$\begin{matrix}C(CH_3)_2\\ \|\\ CH(CH_3)\end{matrix}$

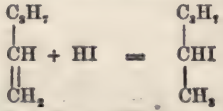
Trimethyl-ethylene.

chloric acid, or a molecule of hypochlorous acid, the double bond is suppressed; the two contiguous carbon atoms, now united by a single atomicity or valency, each fix an atom of chlorine, or an atom of bromine, or an atom of hydrogen, or the group OH; and we may thus imagine isomeric compounds to be produced, according to the place occupied by the atoms fixed in the molecule. Thus the isomerism of the amylene chlorides and bromides, and of the amyl chlorides, bromides, iodides, and hydrates, arises from the isomerism of the amylenes, and we see that all these isomers are accounted for by theory, which shows how they each correspond to a particular atomic grouping. Further, it is important to remember that the formulæ which express this grouping are not chosen at random; they represent facts—that is to say, syntheses, reactions, and decompositions. Thus the formula of propyl-ethylene, (ethyl-allyl) recalls the synthesis of this body by the action of sodium upon a mixture of ethyl iodide and allyl iodide.

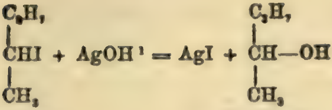
$$\underset{\text{Ethyl iodide.}}{CH_3—CH_2I} + \underset{\text{Allyl iodide.}}{CH_2I—CH=CH_2} + Na_2$$

$$= 2NaI + \underset{\text{Propyl-ethylene.}}{CH_3—CH_2—CH_2—CH=CH_2}$$

The same formula accounts for the transformation of the hydrocarbon in question into an iodide and into secondary amyl alcohol. For greater simplicity we shall here employ the condensed formulæ—



$$\underset{\text{Propyl-ethylene.}}{\begin{array}{c} C_3H_7 \\ | \\ CH \\ \| \\ CH_2 \end{array}} + HI = \underset{\text{Secondary amyl iodide.}}{\begin{array}{c} C_3H_7 \\ | \\ CHI \\ | \\ CH_3 \end{array}}$$



$$\begin{array}{l} C_3H_7 \\ | \\ CHI \\ | \\ CH_3 \end{array} + AgOH\,\text{[1]} = AgI + \begin{array}{l} C_3H_7 \\ | \\ CH-OH \\ | \\ CH_3 \end{array}$$

Secondary amyl iodide. Secondary amyl alcohol.

And this secondary alcohol differs in its properties from two other secondary alcohols which were predicted by theory, and which have been obtained. Thus it differs from the tertiary alcohol, which is formed by the action of water and silver oxide upon amylene hydriodate or tertiary amyl iodide; the latter is the principal product of the action of hydriodic acid upon ordinary amylene. To enable the reader to form an idea of the variety of isomeric compounds which may exist for a relatively simple grouping of atoms, such as that of amyl alcohol, we have given in a note[2] the table of all the known isomers of amyl alcohol. They were predicted by theory and verified by experiment; and this verification of the theory, this happy coincidence between predicted and observed facts, may be noticed in hundreds of cases. Thus far we are justified in the assertion that the notion of atomicity has furnished sure data for the interpretation of isomers.

We shall add but one more example to the preceding developments, which it would be easy, though superfluous, to extend. We have spoken above of primary, secondary, and tertiary amyl alcohols. This is an important conception of Kolbe, and is demonstrated by the following formulæ:—

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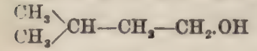
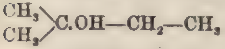
[1] Instead of $Ag_2O + H_2O$

[2] See Note III., p. 336.

$CH_3—CH_2—CH_2—CH_2—CH_2.OH$	normal amylic alcohol, primary.
 $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH—CH_2—CH_2.OH$	fermentation amyl alcohol, primary.
$CH_3—CH_2—CH_2—CH.OH—CH_3$	methyl-propyl carbinol, secondary.
 $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C.OH—CH_2—CH_3$	tertiary amyl alcohol.

Those alcohols are termed primary which contain in the chain of their carbon atoms the group $—CH_2.OH$; secondary, those which contain the group $=CH.OH$; tertiary, those which contain the group $\equiv C.OH$. The primary alcohols alone give on oxidation aldehydes and acids, and the notation accounts for this important fact, for the group $—CH_2.OH$ alone can be converted by oxidation into the group $—CHO$ or into the group $—CO.OH$.[1] Now the group $—CHO$ characterises the aldehydes, and the group $—CO.OH$ the acids.

But what becomes of the secondary and tertiary alcohols when they are subjected to oxidation? One of two things, either their molecule is broken up or it is formed into a corresponding acetone. In the latter case the group $=CH.OH$ is converted into a group $=CO$, which characterises the acetones.[2]

It is evident that the developed formulæ which express the reciprocal bonds between atoms, or, in other words, the atomic chain, account in the most satisfactory manner for the transformations which organic compounds may undergo. They show that a definite atomic grouping corresponds to each *function*, and that the fundamental properties of each class of bodies are in some way dependent upon this particular grouping. We can only give here a general statement of this proposition; its proof would require a volume.[1] In our statement of this proposition, which we have supported by a few examples, we have had but one aim in view —to show that the developed formulæ deduced from the theory of atomicity express facts, and that, when grounded upon the faithful interpretation of reactions, they are of the greatest use in the explanation of cases of isomerism. It is true that such formulæ are somewhat complicated. This complication naturally increases with the number of atoms in the molecule whose atomic grouping we wish to represent. To this we must resign ourselves; the problems which science is called upon to solve are not always simple, and in

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[1] $CH_2—CH_2.OH + O = H_2O + CH_3—CHO.$
Alcohol. Aldehyde.
$CH_3—CH_2.OH + O_2 = H_2O + CH_3—CO.OH.$
Alcohol. Acetic acid.

[2] $CH_3—CH.OH—CH_3 + O = H_2O + CH_3—CO—CH_3$
Secondary isopropyl alcohol. Acetone.

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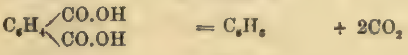
[1] Let us take one from a great number of examples. Acids, we say, contain one or several CO.OH groups. This enables us to explain in a very simple manner the transformation by the action of heat of a great number of acids: the carbonic anhydride which is disengaged comes from the group CO.OH.

$$C_6H_5—CO.OH = C_6H_6 + CO_2$$

Benzoic acid. Benzene.



$$C_6H_4\begin{cases}CO.OH\\CO.OH\end{cases} = C_6H_6 + 2CO_2$$

Benzene.

$$C_6H_4\begin{cases}OH\\CO.OH\end{cases} = C_6H_5—OH + CO_2$$

Salicylic acid. Phenol.

$$C_6H_2(OH)_3—CO.OH = C_6H_3(OH)_3 + CO_2$$

Gallic acid. Pyrogallol.

$$C_6(CO.OH)_6 = C_6H_6 + 6CO_2$$

Mellic acid. Benzene.

the present case the difficulty is in reality small and only likely to repel amateurs of the science. The latter generally ignore the existence of amyl alcohols and isomeric amylenes; their opinion, however, is of little importance, and it would be waste of time to discuss it.

VI.

Constitutional formulæ are based upon the principle of the reciprocal saturation of atoms or of the atomic chain, a principle which follows from the notion of atomicity, of which it is the most important consequence. It has its source in facts, and is of practical utility, for chemists are continually making use of it in discussions relative to the constitution of bodies and to the interpretation of their properties. But it is necessary to make, or rather to renew, a limitation to the signification of these constitutional formulæ. Although they indicate the relations between atoms, they do not pretend to mark their position in space. The latter problem, which relates to the form of molecules, lies beyond the sphere of positive chemistry, although this science may furnish elements for its future solution. An attempt has, however, been made to solve it, so that we are justified in offering a few remarks on the subject.

A molecule formed of two atoms, such as hydrochloric acid, evidently possesses a simple form, which is linear if, instead of considering the atoms themselves, we consider the mean positions of their centres of gravity.

Sodium chloride corresponds to hydrochloric acid, but the molecules of these bodies are only comparable when considered in the gaseous state. When solid or crystallised, sodium chloride is unquestionably formed of several molecules. Supposing that in a cube the eight angular points are occupied by atoms of chlorine and sodium, it would require four molecules of sodium chloride to form an elementary cube of this substance. Similar considerations apply to other solid bodies, which may be formed of aggregations of molecules: dimorphism is explained by the diversity of these molecular aggregations.

A molecule formed of three atoms, such as water, may be constituted in such a manner that one of the atoms—oxygen, for example—being placed at the centre of a circle, the two others occupy the extremity of a diameter.

In ammonia we have four atoms, one of nitrogen and three of hydrogen, and it is probable that the latter are distributed symmetrically round the atom of nitrogen. Considered in their mean positions, all four may be arranged upon one plane, though it may be otherwise.

The case of a molecule formed of five atoms, such as marsh gas or methane, is more complex. The most plausible hypothesis consists in again admitting that the four hydrogen atoms are symmetrically distributed round the carbon atom. The latter may be imagined to be placed in the centre of a regular tetrahedron, of which the four hydrogen atoms would occupy the four angular points.

A few more words upon this hypothesis. It is susceptible of an important development, which we owe to Le Bel and Van't Hoff, and which we now proceed to describe. Speaking correctly, we shall only consider a particular case of a more general proposition enunciated by these chemists; but this simplified demonstration will suffice to give an idea of their conception.

A great number of organic compounds may be derived from marsh gas, regarded as a type of combination.

In fact, the hydrogen atoms may be replaced by other elements, or groups of elements, and especially by carbon groups. An immense variety of combinations may result from these substitutions, and the molecule grows from the complication of the groups in question. But the primitive carbon atom will constitute a kind of nucleus.[1] Suppose that for the four atoms of hydrogen we substitute four identical groups—four ethyl groups, for example—the form of the molecule will be symmetrical, as it was before; and if this form is a regular tetrahedron, a plane passing by an edge and through the centre of the figure occupied by the carbon atom would divide the molecule into two symmetrical halves. This plane of symmetry would comprise two angular points, the two others being situated upon a line perpendicular to this plane and at an equal distance from it.

Let us now suppose that of the four hydrogen atoms of marsh gas two are replaced by groups of atoms, and that the latter are situated upon the plane in question; the two other hydrogen atoms will be situated at equal distances upon a line at right angles to this plane, and, were the plane a mirror, the image of one of the hydrogen atoms would coincide with that of the other. This would no longer be the case if the substitution were extended to a third hydrogen atom, in such a manner that the molecule would now contain three dissimilar elements or groups, R, R′, R″; in this case the elements upon each side of the plane passing through H and R will be R′ and R″, and those situated upon each side of the plane passing through R′ and R″ will be H and R; they are dissimilar in the two cases, and the structure of the molecule will be dissymmetrical. This molecular dissymmetry, thus defined by Le Bel and Van't Hoff, is the cause of rotatory power.

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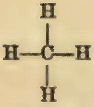
[1] This does not necessarily imply a peculiar condition of the carbon atom.

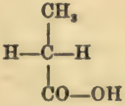
Let us take as examples propionic, lactic, and tartaric acids.

Propionic acid is a bisubstituted derivative of marsh gas.



$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -H \\ & | & \\ & H & \end{array}$$

Marsh gas.

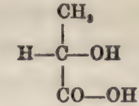


$$\begin{array}{lll} & CH_3 & \\ & | & \\ H- & C & -H \\ & | & \\ & CO-OH & \end{array}$$

Propionic acid.

Let us suppose the molecule to be divided by a plane in such a manner that CH_3, C, and CO.OH shall be situated upon this plane; the two halves will be symmetrical, an atom of hydrogen being situated right and left. Propionic acid does not exercise a rotatory power.

Lactic acid is a trisubstituted derivative of marsh gas of the form

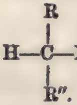


$$\begin{array}{c} CH_3 \\ | \\ H—C—OH \\ | \\ CO—OH \end{array}$$

Lactic acid.

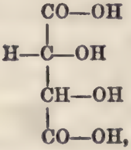
In this case the plane passing through CH_3, C, and CO—OH will no longer be a plane of symmetry, for of the two symmetrical hydrogen atoms which existed in propionic acid one has been replaced by OH; the molecule will therefore be dissymmetrical. Lactic acid exercises a rotatory power.

This is also true for tartaric acid, which may equally be regarded as a trisubstituted derivative of marsh gas, assuming the general form



$$\begin{array}{c} R \\ | \\ H—C—R' \\ | \\ R''. \end{array}$$

Tartaric acid being



$$\begin{array}{l} \quad CO—OH \\ \quad | \\ H—C—OH \\ \quad | \\ \quad CH—OH \\ \quad | \\ \quad CO—OH, \end{array}$$

we see that one of the carbon atoms is united to a hydrogen atom, and to three different groups, R″ being in this case $\begin{array}{l} CH.OH \\ | \\ CO.OH \end{array}$. From what has been said above, the structure of the molecule is dissymmetrical.

The objection will, however, be made that the lactic acid of fermentation is inactive, as are also many other bodies presenting a similar structure. Le Bel sets this difficulty aside by observing that, in a bisubstituted derivative of marsh gas, the third substitution may take place on either side, to left or to right, and that the dissymmetrical compounds thus formed are in reality a mixture in equal proportions of dextro-rotatory and lævo-rotatory bodies, and are consequently inactive.

We may add that the above course of reasoning implies an hypothesis—that, namely, of the fixity of hydrogen atoms and groups, relatively to each other, in the types CHR_2R' and $CHRR'R''$. If this were not so, if the hydrogen atoms and the groups which replace them could be continually changing places in this system and alternately occupy all positions, the molecular dissymmetry, as defined above, could produce no effect, because in the mass of the molecules we should continually find dissymmetrically opposed compounds in equal proportions, and consequently optical neutrality. On the other hand, the grand fact of isomerism demonstrates the stability of the relative positions of atoms and groups for an immense number of combinations. It is well known that to determine, in a given combination, the migration of atoms or groups which produces isomerism, the intervention of a physical force or a chemical agent is necessary—for example, a great elevation of temperature. How could the innumerable isomers of the innumerable derivatives of benzene occur, if the six hydrogen atoms of benzene were not all riveted to their carbon atom, executing in its vicinity, without ever quitting it, as long as the compound exists, those motions which constitute a part of the total energy of the molecule?

We shall confine ourselves to these brief observations, which will at least have shown the cause of the interest which attaches to the attempt of Le Bel and Van't Hoff.

Biot often insisted upon molecular dissymmetry as the cause of rotatory power, and upon the assistance which this remarkable physical property of certain bodies would one day offer to the study of their constitution. This was a prediction which was fulfilled when Pasteur showed the relation which exists between rotatory power and crystalline dissymmetry. But with liquid or dissolved substances it is no longer a question of crystals, but of molecules, and the considerations relative to molecular dissymmetry were, as it were, the offspring of pure chemistry. They have been deduced from the theory of atomicity, and are connected with modern ideas upon the links existing between atoms in combinations.

CHAPTER IV.

HYPOTHESES UPON THE CONSTITUTION OF MATTER.

I.

We have now come to the end of this long exposition, and must conclude.

We have pointed out the origins and followed up the development of this celebrated theory of atoms, which, from the first ages of civilisation, has been present to the human mind, seeking both to penetrate into the inmost recesses of matter and to sound the infinite depths of space. And we have a sound reason for comparing the 'little world' in which atoms are rotating to the great world in which the stars revolve. In both all is motion. We must go back to the very origin of atomism to find this conception of atoms in motion. It is mental power (*νοῦς*) which gives them the impulse, according to Anaxagoras. According to Democrites of Abdera, they are in perpetual motion from their very nature; the force which animates them acts inevitably. They do not differ in their essence—we should now say, in their chemical qualities—but rather in their dimensions, for they have a sensible extension; they differ also in their form. If heavy, they fall into the depths of space; if lighter, they rise in the air. Some have a smooth surface; others present asperities, points, and hooks. The motion which they possess naturally brings them into contact, without their attracting each other; sometimes it masses them together, sometimes separates them. It is in this manner that all things are formed or destroyed. Limited in extent and surface, they cannot be confounded with the medium in which they move. This medium is a vacuum.

Thus we find, at the very origin of atomic ideas, this distinction between 'vacuum and plenum,' or 'vacuity and solidity,' which was maintained for ages, and which appears as one of the solutions which the human mind has been able to give of the constitution of matter. This is the hypothesis of the discontinuity of matter, now generally adopted, with the difference that the vacuum is replaced by a very rarefied, elastic, vibrating medium—ether.

Another hypothesis is that of continuous matter filling all space, with different degrees of density. Descartes inclined towards the latter hypothesis. Dimension being the essential property of bodies, there cannot be bodies without dimensions, which excludes the idea of indivisible particles—that is to say, of atoms. There is no dimension without body, consequently no vacuum.

The same conception follows from the dynamic hypothesis professed by German philosophers at the commencement of this century. Whether, after Kant, matter exists by itself, or is endowed with two contrary forces, one attractive and the other repulsive, or results solely from the conflict of these two forces, as Schelling supposed, it is continuous, and consequently infinitely divisible. Chemical combination results from the mixture of heterogeneous bodies, which penetrate each other, and this penetration is so intimate that we cannot find in the compound either the properties or even the substance of the components ; a new substance is formed, and the smallest particle of it is entirely identical with the whole mass.

We are now struck with the vagueness of the dynamical ideas of Schelling. No force can exist independently ; it must emanate from something or must be applied to something which exists apart from it, and should manifest its presence by motion. How can we conceive motion without a moving body ? For this notion of force, which is, moreover, difficult to define, we may substitute that of motion. In the hypothesis of the continuity of matter the mass which fills the entire universe is in a permanent state of vibratory motion. Waves are transmitted through it in different directions and cross each other, as the waves produced on the surface of water are transmitted and cross with other waves. From the intersection of the waves result nodal surfaces and nodal points, and consequently the limited portions of matter. The diversity of matter would result from the diversity of the systems of waves which traverse it, and we can logically conceive that these portions thus limited, these vibrating slices, these concamerations, if we may use the word, represent the particles of matter which enter into conflict in chemical reactions.

This is an hypothesis, and it seems vague and to possess but slight plausibility, at least under this form. It is otherwise with a conception of Sir William Thomson, who has recently given a striking definition of these limited portions of matter vibrating in the midst of a continuous medium. This definition we shall explain further on.

II.

We will, however, consider more closely the hypothesis of the discontinuity of matter which would be formed of molecules and atoms in motion, in a medium which fills the entire universe and penetrates all bodies—the ether.

Atoms are not material points; they possess a sensible dimension, and doubtless a fixed form; they differ in their relative weights and in the motions with which they are animated. They are indestructible and indivisible by physical and chemical forces, for which they act, in some manner, as points of application. The diversity of matter results from primordial differences, perpetually existing in the very essence of these atoms and in the qualities which are the manifestation of them.

Atoms attract each other, and this atomic attraction is affinity. It is doubtless a form of universal attraction, but it differs from it in that, if it is obedient to the influence of mass, it depends also on the quality of the atoms. Affinity is elective, as has been said for a hundred years. It gives rise to aggregations of atoms, to molecules and chemical combinations. In the latter the atoms are no longer free in their motions; they execute their motions in a kind of coordinated manner, and constitute a system in which everything is solid and in which they are under control. This is a molecule. It has a determinate mass, a centre of gravity, and its peculiar motion. The energy of these molecular motions determines a very important physical condition—temperature. We shall return to this point later.

Ether is not a vacuum; it is a medium formed of a highly rarefied and elastic matter, agitated by perpetual vibrations which are transmitted from atomic matter to the ether, and from the ether to atomic matter. Is it a homogeneous, continuous medium? is it formed of atoms of a second order, a kind of monads, which would form by their aggregation ponderable matter itself? This is a question which can be brought forward, but which cannot be solved. Poisson inclined towards the hypothesis of the discontinuity of the ether; it seemed to him difficult to admit that luminous vibrations could be propagated transversely in a continuous medium. Such as it is, this imperceptible and imponderable medium has, nevertheless, a density, and, after a revived hypothesis of Lesage—that of transmundane atoms—it is the influence of this fluid which would cause the stars of the visible world to gravitate towards each other.

The medium, therefore, extends between all parts of the universe. As a transmitter of radiations it receives and transmits to us, under the form of light and heat, the radiations—that is to say, the vibrations—impressed upon it by the sun and the most distant stars, and sends into space those which proceed from our solar world. And the same exchange is established in the infinite domain of the infinitely small. The atoms and the molecules which move with different velocities in this impressionable medium communicate to it a part of their energy, which is propagated through it under the form of radiant heat and light; and, reciprocally, the calorific and luminous waves of the ether which graze the surface of atoms or groups of atoms augment the amplitude of their trajectory and the energy of their vibratory motions. It is this incessant communication of motions, this perpetual exchange of energy between the ether and atomic matter, which gives rise to the most important phenomena of physics and chemistry.

Among such a varied class of phenomena the hypothesis of atoms establishes relations which no other theory has foreseen, and which are so simple and so well known that it is almost superfluous to mention them.

Take a crystal. Under the microscope its mass appears compact and homogeneous. In its faces and cleavage planes there is no absence of continuity. And, nevertheless, matter is not continuous in it, and, if the substance is a compound, it is not homogeneous. The smallest fragments of the crystal are formed of aggregations of innumerable molecules, which are similar in nature and similarly arranged. Each of these molecules is formed of atoms, varying in number. They are situated at distances sensible compared with their dimensions, and they vibrate in a coordinated manner, forming systems in equilibrium, each of which is animated with determinate motions and is in accord with systems of the same kind. If the body in question is a solid, the atomic systems—that is to say, the molecules which constitute it—preserve their respective positions, and are linked together and fixed with regard to each other, although each one has its own orbit and a certain liberty of motion. It is cohesion, we say, which retains the molecules in their spheres, and affinity which retains the atoms in the narrower limits of the molecule. But these forces are perhaps fundamentally of the same nature: only they act at different distances, and, under the influence of the same causes, they are manifested differently, one giving rise to physical phenomena, the other to chemical phenomena, the latter only being in some manner the continuation of the former.

If we apply heat to a solid body[1] formed of molecules thus constituted, it can produce, independently of external work, three different effects—

Firstly, an elevation of temperature, owing to the increase of the molecular vibratory energy;

Secondly, augmentation of volume from the increase in the space between atoms and molecules, and, if this increase becomes considerable, a change of state: the solid becomes a liquid, the liquid a gas. In the latter case the separation of the molecules has become considerable compared with the dimensions of the latter.

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[1] See note on p. 338.

But, whatever may be the physical effect produced in this order of phenomena, the heat which has disappeared as such has performed work; the vibratory motion which has been communicated to the molecules under the form of heat has succumbed in the struggle against the molecular forces, or, in other words, has performed work represented by dilatation, diminution of cohesion, and change of state.

The phenomena which we have just analysed are physical ones. Chemistry also comes in play; for, in the third place, heat, acting on the atoms themselves which make up the molecule, increases their trajectories, so that the equilibrium which existed in the system is destroyed, and the atoms of one given system pass into the sphere of action of the atoms of another system. From this rupture or this conflict new systems of equilibrium result—that is to say, new molecules. This gives rise to phenomena of dissociation or of decomposition, and inversely of combination, which belong to the domain of chemistry; as is seen, and as we have mentioned above, they are only the continuation of the physical phenomena, the same hypothesis—that of molecules formed of atoms—applying to each with equal simplicity.

It is heat which sets the atoms in motion; they have absorbed heat in separating from each other, since the rupture of the molecular equilibrium which marks the end of the state of combination has required the consumption of a certain quantity of heat. The heat thus absorbed has restored to the atoms the energy which they possessed before combination and which represents affinity. This heat is lost again whenever the atoms, passing into the sphere of action of other atoms, fix the latter in some manner or are fixed by them, so as to form new systems of equilibrium—that is, new molecules—in which henceforth their vibration and motion are preserved. This action is reciprocal; the new combination can only be formed on the condition that the motions of the atoms which constitute it adapt themselves in some manner to each other and harmonise, losing thereby part of their vibratory and potential energy. Hence the disengagement of heat. It is also evident that this adaptation should require certain conditions of modality. All kinds of motion cannot agree in the same manner, and the harmony of the molecular motions should be influenced by the manner of the atomic motions. This circumstance, added to the differences inherent in the very nature of atoms, determines the variety of the systems of equilibrium, or, in other words, the different forms of combination. There intervenes a peculiar property of atoms, very different from their chemical energy. In order to distinguish it from affinity we have called this property of atoms atomicity, and we suppose that it is connected with their very nature and kind of motions.

But are not all these vibratory and rotatory motions which continually agitate molecules and atoms, to which may be added the sliding motions of liquids and the rectilineal progression of gases, so many causes of instability to the molecular systems? The case is the contrary. If they are immovable the atomic aggregations will be more unstable than when they are in motion; the familiar example of the bicycle shows the influence of motion upon the stability of equilibrium.

III.

We have mentioned above the differences inherent in the very nature of atoms and in their manner of motion as determining the form and nature of chemical compounds. The molecular movements have lately been the object of important researches, principally upon the physical constitution of gases, which have resulted in unexpected revelations not only upon the movements and velocities, but even upon the reciprocal distances and absolute dimensions of the ultimate particles. Is this an illusion, a scientific fantasy? No; it is a serious undertaking, a powerful effort made by the most eminent physicists and geometricians, and appears to us worthy of attention, though the future may demonstrate its insufficiency. We will close this exposition with some words upon the subject, warning the reader that we are here entering the invisible world, unassailable by direct experiment, but add that the hypotheses which give us access to it can be verified in some of their consequences and hence acquire a certain degree of probability.

Daniel Bernouilli was the first to bring forward the idea that gases are formed of small material particles, animated with very rapid rectilineal motion, and that the tension of elastic fluids resulted from the impact of their molecules against the sides of the vessels in which they were contained. This is the origin of the kinetic theory of gases, which has been taken up by Herapath, Joule, and Krönig, and the principal author of which is Clausius. Clerk Maxwell has added very important developments to the theory.

Mariotte's law follows as a natural consequence of this hypothesis upon the constitution of gases. If a gaseous mass, composed of an immense but determinate number of particles, is contained in a closed space—the cylinder of an air pump, for instance—the pressure exerted upon the piston will be determinated by the normal components of the impact of the molecules during a unit of time. If the volume of this gas is reduced the number of particles will increase, as well as the number of impacts: the pressure will, therefore, undergo a proportionate increase.

The volume remaining constant, the pressure will be also increased by an elevation of the temperature. Under these conditions the number of the particles remains the same; their masses remain constant, but their velocities, and consequently the number of impacts, is increased, and it is precisely the *vis viva* or the total energy of the molecular motions which give a measure of the temperature.

After the preceding it is evident that a relation exists between the pressure or the tension of a gas and, on the other hand, the velocities of its molecules, their individual mass, and their number in the unit of volume. For these latter factors we may substitute the notion of density, which is the mass of the unit of volume. We see, therefore, that the absolute velocities of the molecules can be calculated from the pressure and the density.

These calculations have been made by Clausius. According to him the molecules of air move with a mean velocity of 485 metres per second, and the molecules of hydrogen with a mean velocity of 1,844 metres. A body projected vertically upwards with a velocity of 485 metres per second would reach a height of 12,000 metres before falling.

Can the gaseous molecules which move with such velocity pass freely over such enormous distances? No; their number is so immense that at every instant they come into contact, encounter each other, and rebound, so that in a gaseous mass formed of molecules of the same kind the latter move in every direction with variable velocities and, between two encounters, in sensibly rectilinear directions. What happens when a gas thus constituted is mixed with another on which it has no chemical action? The molecules of the two fluids begin to diffuse into the space opened to them; preserving their velocities, they encounter each other, so that the sum of their impacts represents the total pressure excited by the mixture. In other words, the pressures of the two gases are added together. This is Dalton's law, which also follows as a natural consequence from the hypothesis of Daniel Bernouilli.

The gases just considered are perfect gases. Their molecules, freed from all cohesion, exert upon each other neither attraction nor repulsion, and, if they encounter each other, it is chance which brings them together. But in reality perfect gases do not exist.

When gaseous molecules approach to within very small distances of each other, cohesion begins to exert a sensible influence, which is transitory, since it decreases very rapidly with the distance. This is the cause of the departures from Mariotte's law and of the inaccuracies of Dalton's law. It is also the cause of slight flexions in the molecular paths, when the particles are on the point of touching.

The preceding considerations are of a physical nature and apply to molecules. The latter may be formed of several atoms, retained by affinity in their reciprocal spheres of action: these atoms have their own peculiar motions, their own energy in the system of which they form a part, and are constrained to move with it in the molecular paths.

The mean molecular velocities[1] are different for different gases at the same temperature; the rectilineal paths passed over between two successive paths are also different. The authors of the kinetic theory of gases—Clausius and Clerk Maxwell—have attempted to calculate the mean lengths of these paths and the number of impacts during a unit of time. These numbers can be determined in absolute value, if certain factors given by experiment are introduced into the calculation. One of these factors is the coefficient of friction of gases.

A gaseous mass which is in motion upon the surface of a solid body tends to transmit, by a kind of friction, a portion of its motion to this body. This causes a retardation of the motion of the gaseous particles in the layer which is immediately in contact with the solid body: this has been termed the external friction. But the layer in question undergoes in its turn a kind of impulse from the neighbouring layer, which is moving faster and which transmits to it a portion of its motion as a mass. Retardation, therefore, takes place on one side and acceleration upon the other: this has been termed internal friction. But this transmission of motion cannot take place without loss, a portion of the motion of the mass being converted into calorific motion. All friction causes a disengagement of heat, and the calorific motion is characterised by the molecules moving in every direction, while they are impelled in the same direction in a gaseous current. The internal friction which the different layers of a gas in motion exercise upon each other gives rise, therefore, to a disengagement of heat—that is to say, to an acceleration of molecular motion. This transmission of motion can only be produced by the impact of the molecules, and we see that a relation exists between the internal friction of gases on one side and the number and energy of the impacts during the unit of time on the other. The number of the impacts itself depends upon the velocity and the distances passed over by the molecules between two impacts. In a word, the coefficient of friction of gases, which has been determined by experiment, can be expressed in terms of the density of the gas, of the molecular velocity, and of the distances passed over between two impacts—that is to say, of the molecular paths. The latter can, therefore, be calculated. Without giving here the numbers obtained for the different gases, we will only mention that the distance passed over by a molecule of air, at the temperature of 0° and under the normal pressure, has been determined—an average and approximate value, since air is a mixture—as equal to ninety-five millionths of a millimetre, which is about twenty-five times smaller than the smallest magnitude visible under the microscope. The number of impacts received by such a molecule during one second will be 4,700 millions, supposing it to move with a mean velocity of 447 metres.

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[1] We shall consider here the *mean* velocities, and add that in a homogeneous gaseous mass—that is to say, in a mass formed of the same kind of molecules—all do not move with the same velocities; in reality, there are some which are endowed with very different velocities. This has been established by Clerk Maxwell.

We may go further. The knowledge of the velocities which animate the molecules and the number of impacts has made it possible to draw inductions upon their distances, their diameters, and their volumes, for is it not true that the lengths of the molecular paths depend upon the frequency of the impacts, and that the latter is influenced by the size of the projectiles? We will not here quote numbers, and will only point out the course of ideas.

Other considerations have been made use of for the approximate determinations of molecular diameters—in the first place, the density of a gas and that of the liquid resulting from its condensation. Loschmidt, Sir William Thomson, and Clerk Maxwell have been engaged upon this question. We will give a word of explanation upon this subject.

If we could suppose that gaseous molecules were brought into contact by liquefaction, the relation existing between the real volume occupied by the material molecules in the unit of volume of a gas and this volume would evidently be given by the relation between the densities in the gaseous and liquid states. This is the relation which Loschmidt terms the coefficient of condensation. Now, the molecular diameter[1] can be expressed in terms of this coefficient and of the mean length of the molecular paths—that is to say, in terms of two known quantities. It is certain that the values calculated in this manner would be too high and rather represent a superior limit, for the supposition that liquefaction brings the molecules in contact is evidently an inexact one. These values are, therefore, only approximate. It is nevertheless a remarkable circumstance that the numerical results obtained in this manner have been confirmed in a satisfactory manner by means of a very different method which has been recently employed by Van der Waals.

This physicist has attempted to determine the molecular magnitudes, taking as his starting-point the departures from Mariotte's law. We have said above that the cohesion of gases is one of the causes of these departures; the material extent of the molecules is another, for it is evident that the space in which the molecules can execute their evolutions is not the same in reality as that occupied by the gas itself; it differs from the latter by the whole extent of the molecular volumes. It is conceivable that the experiments of V. Regnault upon the compressibility of gas might furnish data for the calculation of a constant representing the material extent of molecules, one of the causes of the departures from Mariotte's law. The same constant has been calculated by Van der Waals from the variations of the coefficient of dilatation, and the values obtained have been a little lower in this case. The values in question deal with millionths or with fractions of millionths of a millimetre. This kind of magnitude would express the diameters of molecules and also their respective distances. Let us remark that this scale is nothing extraordinary for physicists. Are not the lengths of light-waves expressed in millionths of a millimetre? And in this connection we should remember that Cauchy has some time ago drawn attention to the fact that the distance between molecules in a refracting medium should be in relation with the wave-lengths. He has shown that dispersion—that is to say, the decomposition—of white light into the different colours of the spectrum could not take place if the material particles of a refracting body were separated by distances infinitely small in relation to the wave-lengths. These distances and these lengths should be magnitudes of the same order.

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[1] We are here treating not exactly of the diameter of the material molecule, but of the radius of what Clausius calls the molecular sphere. The molecular sphere is the portion of space which belongs to the molecule, and within which no other molecule can penetrate.

These molecular spheres of action would occupy, according to Clausius, a volume eight times as great as the molecules themselves. Let us quote some numbers to render these ideas intelligible. Clausius admits that in a cubic centimetre of air the material molecules only occupy a third of a cubic millimetre—that is to say, the 3000th part of the total space—and that the molecular spheres of action occupy about the 400th part of it.

But let us return to gases. The data obtained for the diameters of molecules have made possible the approximate calculation of their sections and of their volumes. For air the two values are only small fractions, the first of a square, the second of a cube, whose side would be the millionth part of a millimetre.

We can go a step further: the molecular volumes being known, we can calculate the number of molecules in the unit of volume of gases, and also their respective distances and their absolute weight. We here arrive at numerical results which confound the imagination, and the real signification of which we have some difficulty in seizing. A cubic centimetre of air would contain twenty-one trillions of molecules, a number which represents twenty-one times the cube of a million.[1] In accordance with the law of Avogadro and Ampère, this number would be the same for the other gases. Suppose gas to be so rarefied that its pressure was reduced to a thousandth part of an atmosphere: the number of molecules contained in it would still be prodigious, although it would only be the thousandth part of the preceding. Only in this rarefied air the molecular paths would be notably elongated, and the number of impacts diminished in proportion. This furnishes an explanation of the possibility of the motion of the radiometer.

The atomic weights, which we have treated at length in this work, only express ponderal relations. These weights can be expressed in absolute value by taking as the bases of the calculation the data acquired upon the dimensions of molecules, and taking into account the densities. If we say that it requires ten trillions of molecules of air and 144 trillions of molecules of hydrogen to make a milligramme of these respective gases, shall we be giving any idea which the mind can grasp, and, above all, will the idea of the values be exact? This may be doubted. Nevertheless these numbers have been given. They are given with reserve, as provisional information upon the limits which the divisibility of matter can reach.

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[1] That is to say, 21 followed by eighteen cyphers. Since the words billion and trillion do not always receive the same meaning, I have thought this explanation necessary

Besides, these approximate results upon the dimension of the material particles and upon the density of this molecular dust which constitutes gases are confirmed, up to a certain point, by well-known facts. An inappreciably small weight of musk is sufficient to perfume the air of a whole room, and Kirchhoff and Bunsen have proved that the three-millionth part of a milligramme of sodium chloride is sufficient to give a yellow colour to a gas jet; and, in another kind of phenomena, Hofmann has found that rosaniline gives a perceptible colour to 100 million times its weight of alcohol. We should also remember that Faraday prepared sheets of gold the thickness of which he estimated as equal to the hundredth part of the length of a light-wave; and, supposing that such a sheet contains a simple layer of molecules, the thickness of one of these could not exceed five millionths of a millimetre, a value comparable to those mentioned above. Everyone is familiar with a soap bubble, but it is difficult to form an idea of the extreme tenuity of the film. In the soap films made by Plateau they scarcely reach a millionth of a millimetre. Sir William Thomson, who has studied this question, has shown by calculation that it is impossible for such a film to contain more than one layer of molecules, which would give for the diameter of these molecules a value inferior to that just mentioned, but which belongs to the same kind of values. Finally, a last and very ingenious method for estimating the limit of the divisibility of matter has been conceived by Sir William Thomson. It consists in determining, by means of his electrometer, the voltaic attraction between a sheet of zinc and a superposed sheet of copper. This attraction is independent of the thickness of the sheets, and can be estimated by the work performed by the sheet of zinc in lifting itself towards the sheet of copper. If thin layers of zinc and copper were made into a pile, this work would increase in consequence of the number of sheets accumulated in a given thickness. This mechanical work can be calculated in heat, and we can calculate the thickness which it would be necessary to give to the sheets for the work performed by a pile of sheets one centimetre in thickness to represent exactly the quantity of heat disengaged by zinc and copper in forming an alloy. In other words, we can calculate the tenuity which it would be necessary to give to the particles of zinc and copper in order that their reciprocal action should only disengage the quantity of heat which is actually observed in the formation of an alloy. The result is as follows: The thickness of these sheets cannot be reduced beyond the thirtieth of the millionth part of a millimetre. It is approximate, for there are uncertainties in the calculation, and it is an inferior limit; but it is noteworthy that we still remain in the order of values deduced from the kinetic theory ot gases.

IV.

This theory, and especially the law of Clerk Maxwell upon the distribution of velocities in gaseous molecules, are founded upon the mathematical laws of the impact of elastic bodies. Are molecules, then, projectiles endowed with elasticity? The admission would be difficult if we wished to maintain the conception, which Newton arrived at, of hard atoms, incapable of altering their form. The difficulty is not diminished if we retain the hypothesis of molecules formed of atoms held together by affinity; and these are exactly the molecules which we have considered in gases as moving in every direction and encountering each other. Are they endowed with elasticity by reason of the extension of their sphere of action beyond their natural limits, according to the ideas of Clausius? Are they surrounded with an envelope of ether? So it has been said, but who can affirm anything in the matter? And then there is a final difficulty. This invisible world, in which it has been attempted to penetrate by an effort which is an honour to the human intelligence, has finite dimensions. It does not exist in absolute quantity, and in this unheard of diminutiveness there are relative magnitudes. Chemistry teaches us that a molecule of mercury weighs 100 times as much as a molecule of hydrogen. Is it, therefore, a great molecule relatively to the other, and why is it indivisible? I do not understand; I do not pretend to do so; only I admit that physical and chemical forces cannot divide it any further, because otherwise it would cease to be mercury. It is not less true that this proposition of the indivisibility of atoms is not to my mind satisfactory, and I am obliged to confess that a difficulty exists here.

In these later times a theory has arisen which seems to give a mathematical demonstration, and even an experimental illustration, of the indivisibility, or rather of the peculiar and eternal individuality, of atoms: I refer to the vortex atoms of Sir William Thomson.

Chemists can form an idea of this vortex motion by recalling to mind the rings which rise in still air whenever a bubble of phosphoretted hydrogen bursts upon the surface of water, and the rings which certain smokers are able to make are familiar to all. An apparatus has been constructed by which they may be produced at will. It is a wooden box one side of which is furnished with a circular opening and the other formed of a tightly stretched cloth. In the interior of the box fumes of sal ammoniac are produced, which are driven out by a sharp blow on the elastic side. A ring of smoke is then seen to issue from the opening and to move freely through the room. In this ring all is motion, and, independently of the motion of translation, the smoke particles roll over each other and execute a rotatory motion in every section of the ring. These motions take place from the interior towards the exterior of the ring, in the direction of the motion of translation, so that the entire mass of air, or of the smoke which forms the ring, revolves continually round a circular axis, which forms, as it were, the nucleus of the ring. There is this remarkable fact in this rotatory motion, that all the particles which are situated upon one of the curves which can be drawn in each section of the ring are indissolubly tied down to their circular paths, and can never quit them; so that the whole mass of the vortex ring will be always formed of the same particles. This theorem was proved by Helmholtz in 1858. This eminent physicist has analysed the vortex motions which would exist in a perfect fluid free from all friction. He has proved that in such a medium vortex rings, bounded by a system of vortex lines,[1] are formed of an invariable quantity of the same liquid molecules, so that the rings can move, and even change their form, without the connexion of their constituent parts ever being broken. They will continue to revolve, and nothing will be able to separate them, divide them, or destroy them. Those existing in the liquid will exist there for ever, and new ones can only be excited in it by a creative act.

The smoke rings of which we have spoken above would give a perfect representation of these liquid vortex rings, if they were formed and moved in a perfect fluid. They are not so; but such as can be formed can serve for the demonstration of some properties of matter in vortex motion. They are endowed with elasticity and can change their form. The circle is their position of equilibrium, and, when their form is altered, they oscillate round this position, and finally reassume the circular form. But if we try to cut them they recede before the knife, or bend round it, without allowing themselves to be injured. They give, therefore, a material representation of something which would be indivisible. And when two rings meet each other they behave like two solid elastic bodies; after the impact they vibrate energetically. It is a singular fact that when two rings are moving in the same direction, so that their centres are situated upon the same line and their planes perpendicular to this line, the hinder ring contracts continually, whilst its velocity increases; the ring in advance, on the contrary, expands, and its velocity decreases until the other has passed it, when the same action recommences, so that the rings alternately pass through each other. But, through all these changes of form and velocity, each preserves its own individuality, and these two circular masses of smoke move through the air as if they were something perfectly distinct and independent. These curious experiments were made in England.[1]

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[1] 'Wirbelfäden und Wirbellinien.'

Helmholtz, therefore, has discovered the fundamental properties of matter in vortex motion, and Sir William Thomson has stated: This perfect medium and these vortex rings which move through it represent the universe. A fluid fills all space, and what we call matter are portions of this fluid which are animated with vortex motion. There are innumerable legions of very small fractions or portions, but each of these portions is perfectly limited, distinct from the entire mass, and distinct from all others, not only in its own substance, but in its mass and its mode of motion—qualities which it will preserve for ever. These portions are atoms. In the perfect medium which contains them all, none of them can change or disappear, none of them can be formed spontaneously. Everywhere atoms of the same kind are constituted after the same fashion, and are endowed with the same properties. It is well known, in fact, that the atoms of hydrogen vibrate exactly in the same periods, whether we heat them in a Geissler's tube, observe them in the sun, or in the most distant nebulæ.

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[1] P. G. Tait, *Lectures on some Recent Advances in Physical Science.* London, 1876.

Such is, in a few words, the conception of vortex atoms. It accounts, in a satisfactory manner, for some properties of matter, and of all the hypotheses upon the nature of atoms it appears to be the most probable. We see also that it permits the revival of the ancient hypothesis of the unity of matter, and in a more acceptable form than that of Prout's hypothesis. Is the idea absolutely new? No; it was originally conceived by Descartes. So far is it true that, when the perpetual, and perhaps insolvable, problem of the constitution of matter is discussed, the human mind seems to turn in a circle, the same ideas lasting for ages, and being presented under fresh forms to the highest intellects who have endeavoured to solve this problem. But is there no difference among these great intellects in their manner of working? Most certainly: some, more powerful perhaps, but bolder, have proceeded by intuition; others, better armed and stricter, by induction. Here lies the progress and the superiority of modern methods, and it would be unjust to pretend that the important efforts, of which we have had striking testimony, have not made an advance in this difficult problem which was impossible to Lucretius and even to Descartes.

One word more before concluding.

We have been able to see, from the preceding, that atoms are limited portions of matter in motion, whatever may be the idea which we take of their nature and of their form. Since heat itself is a mode of motion, it results that thermo-chemical facts agree perfectly with the atomic hypothesis: they follow from it in some manner as a natural consequence. It is, therefore, useless to attempt to bring forward in opposition to the hypothesis of atoms considerations drawn from thermo-chemistry, as furnishing a more solid foundation for molecular dynamics. Far from being opposed, these notions are correlative. The forces which are considered in mechanics must emanate from something, and they must be applied to something. In chemistry we suppose that they emanate from and are applied to imperceptible but limited and definite particles, which represent the fixed proportions according to which bodies combine. We call these particles atoms, endeavouring to interpret the modern and definite notion of fixed and multiple proportions by weight and by volume, by an ancient hypothesis which preserves the character of an hypothesis even under its altered form.

Does this mean that this hypothesis gains our acceptance because it explains so many facts in chemistry and physics? By no means. In its present form it is far from being perfect, and if it interprets in a wonderful manner certain phenomena of weight and measure, which are in reality the very foundation of chemistry, it leaves other phenomena in the shade. The properties of elementary and compound bodies are probably dependent upon the innate nature of atoms, upon their form and their mode of motion. But these matters are uncertain and unknown. That is the reason why, with our imperfect notions of the very essence of atoms, the theory cannot predict the form of compounds or their properties. These are matters of experiment. Now, a perfect theory ought not only to guide experiment, but to anticipate it.

But, whatever may be the kind of hypothesis under discussion, one point is definitely gained, viz. the notation which is called atomic, since a name must be given to it, but which is independent, up to a certain point, of the hypothesis which it recalls.

The present notation is founded upon facts. It sums up and reconciles in some manner the most important discoveries relating to chemical combinations—those, namely, of Richter, Dalton, and Gay-Lussac. It rests especially upon a rigorous application of the law of volumes discovered by the latter and interpreted by Avogadro and Ampère. And, when the law of volumes is at fault, owing to the fixity of the elements or of their compounds, we have recourse to the law of specific heats or the law of isomorphism for the determination of atomic weights and for the construction of formulæ.

The notation which derives its name from the atomic hypothesis rests, therefore, upon the sure foundation of experiment. The same may be said of the considerations upon atomicity. They are founded upon the fact that the forms of combinations are various, as we have learnt, in the first place, from the discovery of multiple proportions by Dalton, and, in the second place, from the discovery by Gay-Lussac of the relations by volume according to which gaseous bodies combine—relations which are simple, but not identical for different gases. The considerations, therefore, upon the valency or the combining value of elements would survive the hypothesis of atoms if the latter were one day replaced by a more general hypothesis. But this day has not arrived; it is useless to attempt to discredit the former as long as it proves itself productive. Its fertility and its power are clearly manifested in the incessant progress of the science. It has thrown light upon the most recent discoveries, as it has been, since the time of Dalton, its immortal author, the most perfect instrument in the most profound theoretical conceptions and the safest guide in experimental researches.

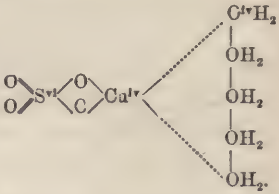
APPENDIX.

NOTE I.

WATER OF CRYSTALLISATION.

THE combination with water of crystallisation is a phenomenon both of a chemical and of a physical order: of a chemical order, since the chemical force, *elective* affinity, plays a part in the phenomenon, and of a physical order, since it is connected with external form and change of state. Let us consider salts, properly so called. Their hydration or their degree of hydration is determined by the nature of the base, rather than by the nature of the acid; for we know that all the sulphates, for example, do not crystallise with the same quantity of water, and that two very similar sulphates—those of potassium and of sodium, for instance—can exist one in the anhydrous, and the other in the hydrated condition. If, therefore, it is the nature of the base which determines the degree of hydration, at least in certain salts, it seems that it is the base also, or rather the metal, which attracts the molecules of water. This attraction may be due to the development of supplementary atomicities in the metal of the salts and in the oxygen of the water. We are now upon a ground riddled with hypotheses. For brevity's sake, therefore, I will take a single example.

Copper sulphate crystallises with five molecules of water. The copper becoming quadrivalent can attract these molecules, supposing the oxygen of the water itself to have become quadrivalent, and we may conceive that the five molecules can be joined together so as to leave at the end of the chain two free atomicities by which the system is attached to the copper. This idea is expressed in the following formula :—



The molecules of water were free ; they are now riveted to one another and to the sulphate of copper : they have lost something, and changed their state by becoming solid, and this double condition has given rise to a disengagement of heat. And let us notice that this chain of molecules of water can be increased, so to speak, at will. In ferrous sulphate, for instance, it is increased by two links. Lastly, the molecules, especially when they are numerous, can fix themselves upon several polyatomic elements in the same compound. This might easily be developed, but I stop : I am satisfied with having stated the idea and given an example.

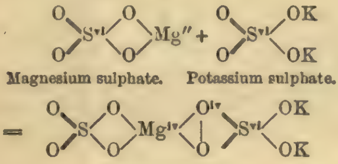
NOTE II.

THE CONSTITUTION OF DOUBLE SALTS.

Let us take as an example the double sulphates of the magnesium series. In order to explain the attraction which sulphate of magnesium exercises upon sulphate of potassium, several hypotheses may be brought forward. The magnesium becomes quadrivalent, and exchanges two valencies either with two atoms of oxygen, or with the atom of hexatomic sulphur of the molecule of sulphate of potassium.

The two molecules are united by the sulphur of one to the oxygen of the other, or, which appears less probable, by the sulphur of one to the sulphur of the other, or by the oxygen of one to the oxygen of the other, the atoms of oxygen becoming quadrivalent. It is not necessary to develope this at length by formulæ which are moreover easy of construction. I here give two of these formulæ, and only add that such combinations between molecules rich in oxygen appear to me to be caused rather by the union, that is to say, by the affinity of heterogeneous atoms, than by the union of atoms of the same nature, as sulphur with sulphur and oxygen with oxygen.

(1.)

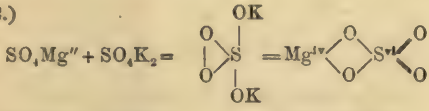


Magnesium sulphate. Potassium sulphate.

Double sulphate.

Here two atoms of oxygen of the potassium sulphate have become quadrivalent, as well as the magnesium of the molecule of magnesium sulphate.

(2.)



Magnesium sulphate. Potassium sulphate. Double sulphate.

Here magnesium, becoming quadrivalent, is attached to the hexatomic sulphur of the molecule of potassium sulphate.

I will not dwell at greater length upon this view, since it is entirely hypothetical.

NOTE III.

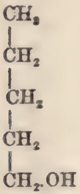
THE ISOMERISM OF THE AMYL ALCOHOLS.

In order to give an idea of the facility with which the theory of atomicity interprets and foretells cases of isomerism, we will here discuss at greater length the isomerism of the amyl alcohols. We were unwilling to introduce it into the text, in order to avoid complicating our explanation.

Primary, secondary, and tertiary alcohols are known (see p. 296). The normal amyl alcohol, discovered by Lieben, and the amyl alcohol of fermentation are both primary. The fermentation alcohol rotates a ray of polarised light to the left. A. Le Bel has recently discovered the amyl alcohol which possesses a dextro-rotatory power. Pasteur made known the inactive variety, which is a mixture of the dextro-rotatory alcohol with the lævo-rotatory alcohol.

The following formulæ express the constitution of these alcohols :—

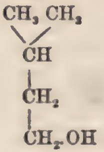
I.



$CH_3-CH_2-CH_2-CH_2-CH_2.OH$

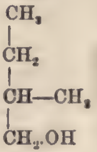
Normal amyl alcohol.

II.



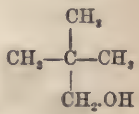
Amyl alcohol of fermentation.

III.



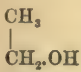
Unknown.

IV.



Unknown.

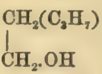
Comparing the constitution of these alcohols with that of ordinary alcohol, we may regard the two first as ethyl hydrate in which one atom of hydrogen of the group CH_3 is replaced by propyl or by isopropyl, the third as ethyl hydrate in which one atom of hydrogen is replaced by ethyl, and another by methyl, and lastly, the fourth as ethyl hydrate in which three atoms of hydrogen are replaced by three methyl groups; this last alcohol corresponding to the trimethylacetic acid of Boutlerow. This point of view is expressed in the following formulæ:—



$$\begin{array}{l}\mathrm{CH_3}\\ |\\ \mathrm{CH_2.OH}\end{array}$$

Ethylic hydrate.

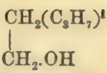
I.



$$\begin{array}{l}\mathrm{CH_2(C_3H_7)}\\ |\\ \mathrm{CH_2.OH}\end{array}$$

Propyl-ethylic hydrate.

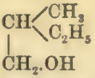
II.



$$\begin{array}{l}\mathrm{CH_2(C_3H_7)'}\\ |\\ \mathrm{CH_2.OH}\end{array}$$

Isopropyl-ethylic hydrate.

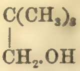
III.



$$\begin{array}{l}\mathrm{CH}\begin{array}{l}\diagup \mathrm{CH_3}\\ \diagdown \mathrm{C_2H_5}\end{array}\\ |\\ \mathrm{CH_2.OH}\end{array}$$

Methyl-ethyl-ethylic hydrate.

IV.

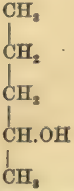


$$\begin{array}{l}\mathrm{C(CH_3)_3}\\ |\\ \mathrm{CH_2.OH}\end{array}$$

Trimethyl-ethylic hydrate.

The secondary amyl alcohols are three in number, viz.—

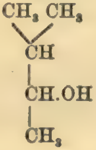
V.



$$\begin{array}{l}\mathrm{CH_3}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CH.OH}\\ |\\ \mathrm{CH_3}\end{array}$$

Boiling point 120°, Wurtz.

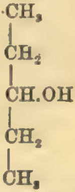
VI.



$$\begin{array}{l}\mathrm{CH_3\ CH_3}\\ \quad\diagdown\diagup\\ \quad\mathrm{CH}\\ \quad|\\ \quad\mathrm{CH.OH}\\ \quad|\\ \quad\mathrm{CH_3}\end{array}$$

Boiling point 108°, Wichnegratsky.

VII.

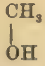


$$\begin{array}{l}\mathrm{CH_3}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CH.OH}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_3}\end{array}$$

Boiling point 116°–117°, Saytzew.

These secondary amyl alcohols can be regarded as derivatives of methyl alcohol in which two atoms of hydrogen are replaced either by propyl and methyl, or by isopropyl and methyl, or by two ethyl groups.

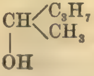
We thus have the simplified formulæ:—



$$\begin{array}{l}\mathrm{CH_3}\\ |\\ \mathrm{OH}\end{array}$$

Methylic hydrate (carbinol).

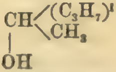
V.



$$\begin{array}{l}\mathrm{CH}\begin{array}{l}\diagup \mathrm{C_3H_7}\\ \diagdown \mathrm{CH_3}\end{array}\\ |\\ \mathrm{OH}\end{array}$$

Propyl-methyl-methylic hydrate (propyl-methyl carbinol).

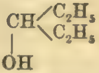
VI.



$$\begin{array}{l}\mathrm{CH}\begin{array}{l}\diagup \mathrm{(C_3H_7)'}\\ \diagdown \mathrm{CH_3}\end{array}\\ |\\ \mathrm{OH}\end{array}$$

Isopropyl-methyl-methylic hydrate (isopropyl-methyl carbinol).

VII.

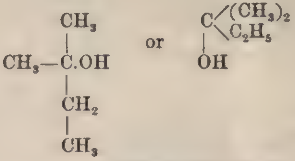


$$\begin{array}{l}\mathrm{CH}\begin{array}{l}\diagup \mathrm{C_2H_5}\\ \diagdown \mathrm{C_2H_5}\end{array}\\ |\\ \mathrm{OH}\end{array}$$

Diethyl-methylic hydrate (diethyl carbinol).

Lastly, a tertiary amyl alcohol is known: it is the body which I have described under the name of amylene hydrate. It contains two methyl and one ethyl groups.

VIII.



$$\begin{array}{l} \quad\quad\;\; CH_3 \\ \quad\quad\quad | \\ CH_3-C.OH \\ \quad\quad\quad | \\ \quad\quad\;\; CH_2 \\ \quad\quad\quad | \\ \quad\quad\;\; CH_3 \end{array} \quad \text{or} \quad \begin{array}{l} C\begin{array}{l}\diagup (CH_3)_2 \\ \diagdown C_2H_5\end{array} \\ | \\ OH \end{array}$$

Tertiary amyl alcohol.

We have given all these formulæ in order to show with what facility the theory of atomicity foretells, limits, and interprets the most complicated cases of isomerism. The principles here developed may be applied to many other examples.

NOTE IV.

THE ACTION OF HEAT UPON GASES.

We have pointed out in the text the manner of action of heat upon the molecules of a solid body. We think it useful to follow up this point by analysing the case of a gaseous body. We know that the heat absorbed by gases produces different effects, whether we heat it under constant pressure or under constant volume. In the first case—

(i.) It increases the external work corresponding to dilatation and to the pressure supported by the gas;

(ii.) It increases the energy of the progressive rectilinear molecular motion;

(iii.) It increases the energy of the atomic motion, and performs certain work within the molecule when the molecule is composed of many atoms.

In the second case, when the gas is heated under constant volume, the first effect is nil. The second and the third are produced, but nothing proves that the internal work is the same under constant pressure and under constant volume. This work disappears in the case of monatomic gases, such as mercury vapour (p. 121). It should increase with the number of atoms in the molecule.

The total energy of a gaseous molecule is composed of the energy of the progressive molecule motion and of the atomic energy (Kinetic and Potential). Clausius admits that a relation exists between the total energy H and the energy of the progressive motion K, and he expresses this relation by the following equation :—

$$\frac{H}{K}=\frac{2}{3}\cdot\frac{1}{k-1},$$

k being the ratio of the specific heats $\frac{C}{c}$ (p. 122). In the case of mercury vapour $H=K$, $k=1{\cdot}666$. In the case of polyatomic gases, the values of k become smaller, for the gases H_2, O_2, and N_2 falling between 1·395 and 1·413. These values decrease as the number of atoms in the gaseous molecule increase.

The absolute zero would correspond to the cessation of the molecular and atomic motions. The temperatures of a gas increase proportionately with the kinetic energy of its molecules; or again, since the masses remain constant, with the squares of the molecular velocities. The heat contained in a gaseous mass is represented by the sum of the kinetic energies of its molecules.

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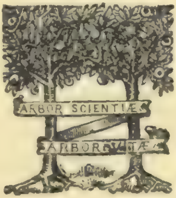

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